

*Chem.  
Thesis case*



THE ACTIVITIES OF THE IONS IN  
SOLUTIONS OF MIXED ELECTRO-  
LYTES WITH COMMON ANION.

Thesis submitted in partial fulfill-  
ment of the requirements for the degree of  
Doctor of Philosophy

By  
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*IV*

C O N T E N T S

	Page
1. Theoretical Consideration . . . . .	1
2. Apparatus and Preparation of Material	4
3. Experimental Results . . . . .	7
4. Conclusion . . . . .	9

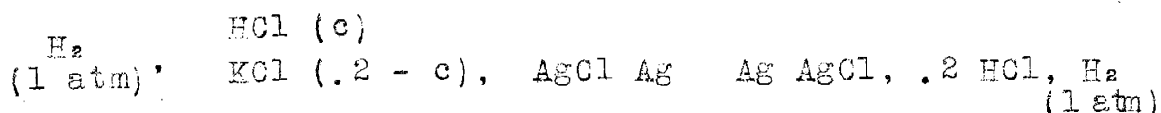
THE ACTIVITIES OF THE IONS IN SOLUTIONS  
OF MIXED ELECTROLYTES WITH COMMON ANION.

I. THEORETICAL CONSIDERATION.

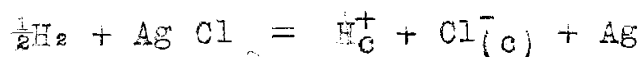
From conductivity measurements it has been found that the equivalent conductance of the chloride ion ( $T_{ce} \Lambda$ ) is the same at a given concentration whatever cation it is associated with. ( $T_{ce}$  equals the anion transference number and  $\Lambda$  equals the equivalent conductance of the salt at the concentration in question. Since the nature of the chloride ion, in this respect, is independent of its source, there appears to be good reason to expect this may also be true in dealing with activity coefficient of the ion instead of the conductivity. To investigate this, I made measurements of the electromotive force of voltaic cells of the type:

$H_2$  (1 atm) HCl  $c_1$  + KCl  $c_2$  AgCl Ag  
in which the separate concentration  $c_1$  and  $c_2$  were

varied in such a way that the sum  $c_1 + c_2$  was always constant, in our case .2 normal. Let us consider such a cell is connected in series and in opposition to a similar cell with .2 n. HCl, thus



When **one** faradays of electricity passes through, in the left cell this change of state takes place



In the right cell this change of state takes place



In other words, one mol of HCl is formed in the left cell and one mol of HCl is removed from the right cell.

The net change is therefore



The free energy decrease attending such a change is

$$-\Delta F = (E_c - E_{.2}) NF = \frac{RT}{N} \ln \frac{A_{\text{H}^+ (.2)} A_{\text{Cl}^- (.2)}}{A_{\text{H}^+ (c)} A_{\text{Cl}^- (c)}}$$

in which  $E_c$  = e.m.f. of cell containing the mixture of

HCl and KCl

$E_{.2}$  = e.m.f. " " " pure HCl at .2 normal

R = gas constant

T = Temperature

F = Faraday of electricity

N = number of faraday of electricity

$A_{\text{Cl}^-}$  = activity of the chloride ion, etc: etc:

Since the activity is equal to concentration times the activity coefficient, the above expression may be written

$$\begin{aligned}
 E_c - E_{.2} &= \frac{RT}{F} \ln \frac{a_{H(.2)} \times .2 \times a_{Cl(.2)} \times .2}{a_{H(c)} \times c \times a_{Cl(c)} \times .2} \\
 &= \frac{RT}{F} \ln \frac{a_{H(.2)} a_{Cl(.2)}}{a_{H(c)} a_{Cl(c)}} + \frac{RT}{F} \ln \frac{.2}{c}
 \end{aligned}$$

By transposition

$$\log \frac{a_{H(.2)} a_{Cl(.2)}}{a_{H(c)} a_{Cl(c)}} = \frac{(E_c - E_{.2}) NF}{RT \times 2.3} - \log \frac{.2}{c}$$

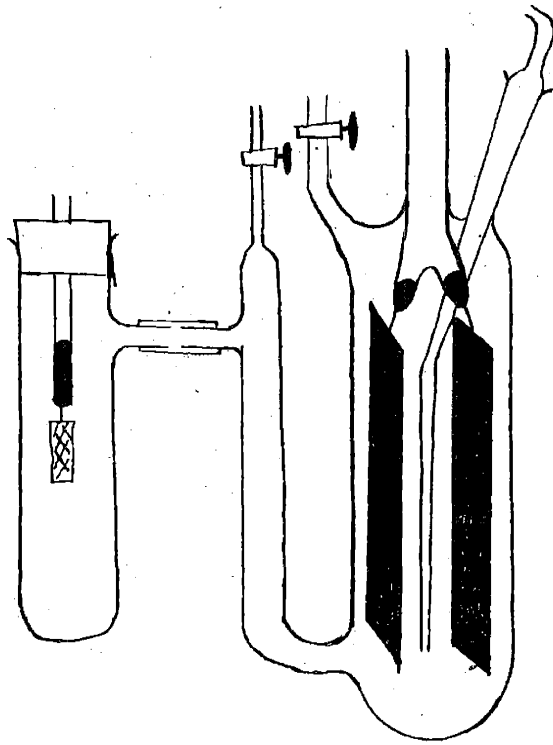
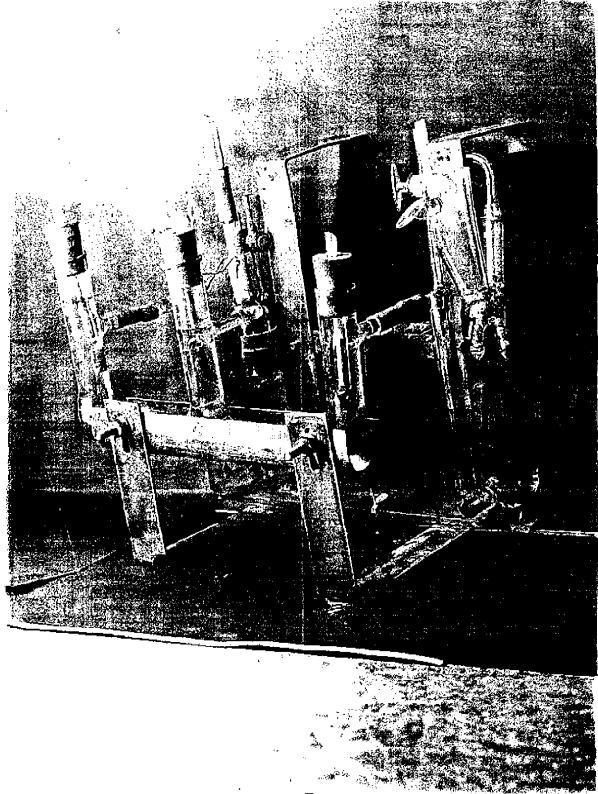
If the principle, that the activity coefficient of HCl at (c) concentration is the same as that of HCl at .2 normal, provided we keep the total concentration of the mixture at .2 normal, is true, then

$$\begin{aligned}
 \log \frac{a_{H(.2)} a_{Cl(.2)}}{a_{H(c)} a_{Cl(c)}} &= 0 \\
 \frac{a_{H(.2)} a_{Cl(.2)}}{a_{H(c)} a_{Cl(c)}} &= 1
 \end{aligned}$$

$$E_c - E_{.2} = \frac{RT}{F} \ln \frac{.2}{c}$$

Such an investigation enables one to draw conclusions in regard to the separate activities of the hydrogen ion and chloride ion.

A similar investigation has been published by Loomis, Essex, Meacham<sup>1</sup> and recently Ming Chow<sup>2</sup> of



this laboratory. Chow's data lead to different conclusions from those of Loomis. At the suggestion of Professor D. A. MacInnes and Professor A. A. Noyes, it appeared that the problem should be further investigated at other concentration than the single one used by Chow.

## 2. APPARATUS AND PREPARATION OF MATERIAL.

The form of the cell is shown in the diagram and photograph. The silver chloride half-cell has three compartments containing three separate silver, silver-chloride electrodes. The silver chloride half-cell is connected with two hydrogen half-cells, a description of which has been given by Noyes and Ellis.<sup>3</sup>

The electrolysis of sodium hydroxide solution furnishes the hydrogen, which is purified by dilute sulphuric acid solution and then bubbled through the same solution as in the cell before reaching the hydrogen electrodes. The electrolytic cell and the <sup>not</sup> forms of the washers are shown in the diagram. It is quite necessary to have a tall electrolytic cell in order to furnish enough hydrogen pressure.

The silver, silver chloride electrode consists of a platinum gauze of about 1 sq. cm. silver plated at about .003 amp. for twenty-four hours, and covered with silver chloride electrolytically at about .007 amp. for one half hour in the solution in which the electrode is intended to be used.

A .2 normal hydrochloric acid solution is prepared by diluting with distilled water (by weight) the constant boiling acid made as described by Hulet and Bonner.<sup>4</sup> This constant boiling HCl acid was prepared and analyzed in March 1918 and recently I repeated the analysis and found an almost identical composition.

A .2 normal solution of potassium chloride solution was prepared. The salt was a Kalbaum preparation recrystallized five times and fused.

The mixtures of hydrochloric acid and potassium chloride were prepared by weighing out definite quantities of the two solutions. This yielded mixtures always containing just .2 molal of chloride ion constituent per 1000 grams of water. The contents in hydrochloric acid and potassium chloride can be calculated from the weights taken.



The cell was immersed in a thermostat of 25°C ± .02°. The electromotive force of the cell was measured by a Leeds and Northrup's potentiometer accurate to .01 mv., the extended wire of which had been recently calibrated.

### EXPERIMENTAL RESULTS

Table I

Concentration of HCl mols per 1000 g. H <sub>2</sub> O	.2000	.16285	.1542	.1058	.05391	.04215
Atmospheric Pressure in mm.	769.6	774.5	766.1	775.4	743.4	744.0
e. m. f.	.31806 .31802 .31797 .31808 .31812 .31802 .31811 .31817 .31811	.32345 .32345 .32340 .32339 .32338 .32333	.32460 .32472 .32467 .32477 .32472 .32486	.33440 .33427 .33456 .33445 .33463 .33427	.35063 .35051 .35050 .35079 .35070 .35067 .35082 .35088 .35085	.35739 .35728 .35730 .35742 .35733 .35736 .35742 .35734 .35735
Average	<u>.31807</u>	<u>.32340</u>	<u>.32472</u>	<u>.33443</u>	<u>.35071</u>	<u>.35735</u>
e. m. f. re- duced to 1 atm.	.31831	.32355	.32502	.33457	.35140	.35803
$E_2 + \frac{RT}{F} \ln \frac{2}{C}$	.31831	.32359	.32499	.33467	.35198	.35831
$\frac{a_{H(.2)}}{a_{H(c)}} \frac{a_{Cl(.2)}}{a_{Cl(.2)}}$		.9988	1.0013	.9964	(.9751)	.9831

### 3. THE EXPERIMENTAL RESULTS

The results of the experiment are tabulated in Table I, which is practically self explanatory. The first horizontal row represents the concentration in mols of hydrochloric acid per 1000 grams of water. Of course there goes with it the corresponding amount of potassium chloride, so that the sum of the concentrations of the two electrolytes is .2 normal. The second row gives the prevailing atmospheric pressure during the measurement of the electromotive force of the cells. The third row represents the actual electromotive force observed. These values are taken after they become stationary for at least two hours. The following table (Table II) will give some idea as to the progress of a representative measurement. We see that as time goes on the value of the electromotive force approaches a definite value (approximately 1.10).

TABLE II

11:35	12:15	1:30
.33442	.33445	.33440
.33430	.33430	.33427
.33445	.33460	.33456
.33442	.33440	.33445
.33440	.33452	.33463
.33445	.33437	.33427

Taken as a whole, each value seldom differs from the average by more than .1 millivolt. This may be attributed to the excellent reproducibility of the silver, silver chloride electrode. This definiteness gives the observer such confidence that he hardly has if he uses calomel electrode, I found from my personal experience with both kinds of electrodes.

I might also remark that the value .31831 for the cell  $\text{AgAgCl} \text{ HCl}(.2) \text{H}_2(1 \text{ atm})$  is almost identical with that interpolated from Dr. Ellis<sup>3</sup> values.

The fourth row gives the values of the electromotive force reduced to one atmosphere, taking into consideration the vapor pressure of the solution, the column of water at the outlet of the hydrogen, and the atmospheric pressure. The vapor pressure of the solution is practically the same as that of pure water (23.5 mm.), since the vapor pressure lowerings, due to the presence of the electrolytes at those dilutions, are entirely negligible.

#### 4. CONCLUSION

From thermodynamic considerations, we derived at the beginning of this thesis, it is seen that

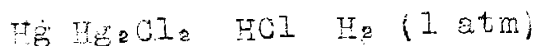
$$(E_c - E_{.2}) = \frac{RT}{F} \ln \frac{.2}{C} + \frac{RT}{F} \ln \frac{a_{H(.2)} a_{Cl(.2)}}{a_{H(c)} a_{Cl(.2)}}$$

By assuming that the activity coefficient of hydrochloric acid at .2 normal is the same as that at C concentration, keeping the total concentration of the two electrolytes constant, the above expression becomes

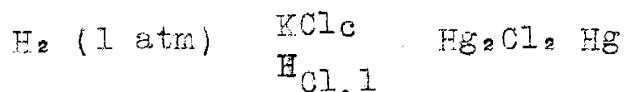
$$E_c = E_{.2} + \frac{RT}{F} \ln \frac{.2}{C}$$

This assumption is adequately proven experimentally as one compares the values of the fourth and the fifth rows of Table I. It must be noticed that the deviations are in both directions. There is no steady progressive deviation, although at .05391 normal concentration there is a big deviation. But at .04215 normal concentration, the deviation is very much less, showing that it is an experimental error rather than a continuous deviation.

Attention has not been called to the fact that the above principle is further supported by the data of Ellis<sup>3</sup> and Harned<sup>5</sup> at .2 normal concentration. Ellis measured the electromotive force of the cell



Harned measured the electromotive force of the cell



keeping the concentration of HCl constant at .1 normal and varying the concentration of KCl. Their results are shown in Table III.

Table III

Ellis		Harned	
Concentration of HCl	e.m.f.	Concentration of KCl	e.m.f.
4.484	.15506	.060	.38911
1.9278	.23589	.100	.38410
1.0381	.27597	.120	.38141
.77137	.29571		
.50948	.31865		
.33757	.33836		
.10040	.39884		
.03332	.45258		

By interpolation Ellis' value is .3661 volt at .2 normal of HCl. The electromotive force of the cell  
 $\text{Hg Hg}_2\text{Cl}_2 .1 \text{ n. KCl} + .1 \text{ n. HCl H}_2$

is .3841 volt.  $E_{.2} + \frac{RT}{F} \ln \frac{.2}{.1} = .38392 \text{ volt.}$

A difference of .00018 volt is not at all big, considering that these experiments are performed by two persons.

Since the strictly thermodynamic expression

$$E_c - E_{.2} = \frac{RT}{F} \ln \frac{A_{H(.2)} A_{Cl(.2)}}{A_{H(c)} A_{Cl(.2)}}$$

can be replaced by the expression

$$E_c - E_{.2} = \frac{RT}{F} \ln \frac{.2}{c}$$

one can readily conclude that the activity of hydrochloric acid is proportional to its concentration if the total chloride ion is kept constant. Since it can hardly be an accident that Ellis' and Harned's data, at .2 normal, agree so well, the above conclusion is a necessary consequence. Furthermore, we see in the sixth row of Table I  $\frac{a_{H(.2)} a_{Cl(.2)}}{a_{H(c)} a_{Cl(.2)}}$  is practically unity in all mixtures.

If we accept the theory by Professor MacInnes<sup>6</sup> that the chloride ion, no matter whether it is associated with hydrogen or potassium ion, has the same activity in solutions in which the chloride concentration is the same, then the hydrogen ion has an activity proportional to its concentration. Of course this is only true when the total chloride ion concentration is always constant. If the chloride ion from the HCl has a different activity from the activity of chloride ion in KCl, then they must vary in every mixture in such a way that they just compensate the varia-

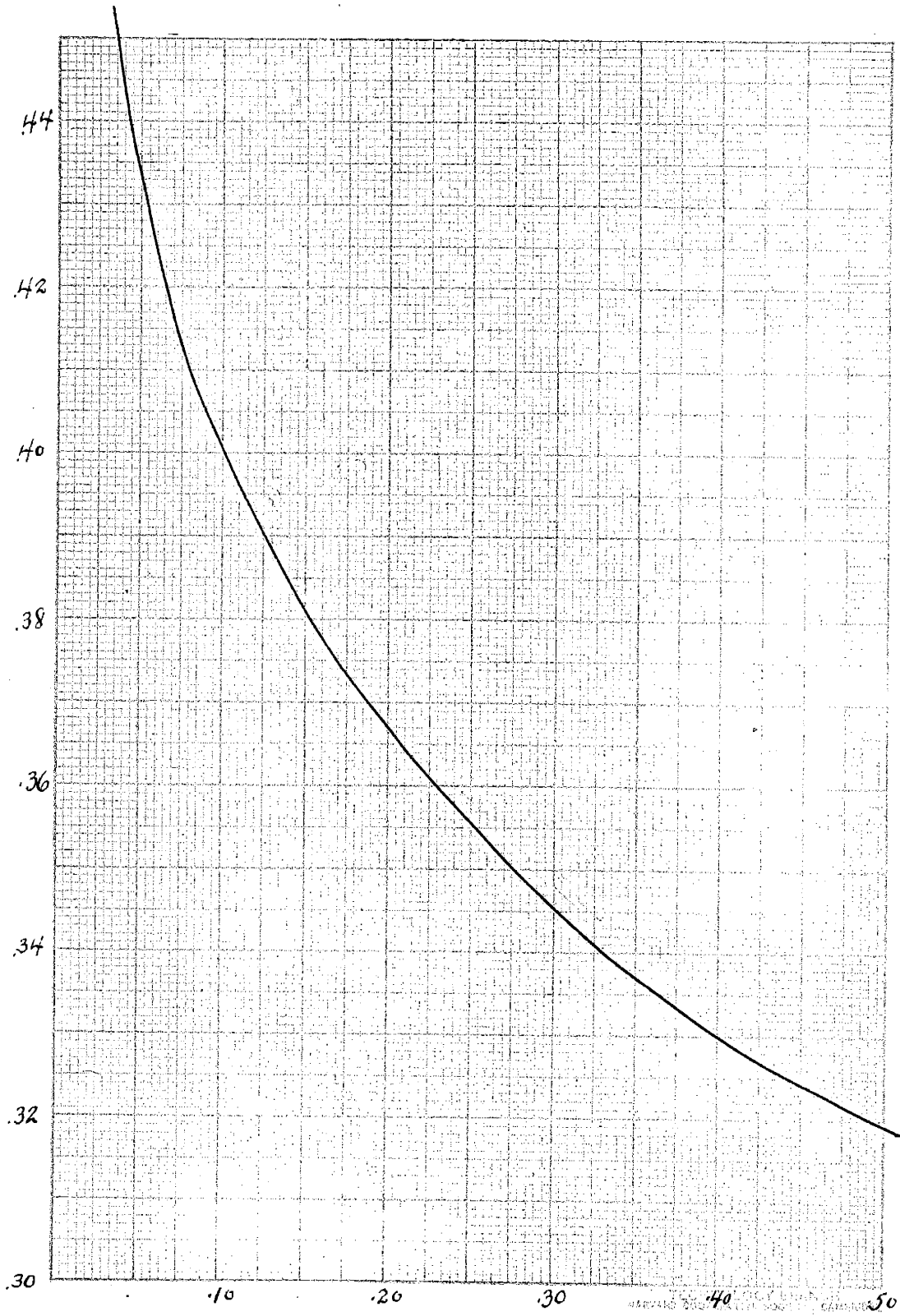
tion of the ratio  $\frac{a_{H(2)}}{a_{H(c)}}$  in order to make

$\frac{a_{H(.2)} a_{Cl(.2)}}{a_{H(c)} a_{Cl(.2)}}$  equal to unity. Such kind of

peculiar coincidence is very improbable.

Finally I might mention that at higher concentrations Ellis and Harned data show wide deviation from the above principle.

EMF in volts



EMF in volts

Concentration of HCl



R E F E R E N C E S

1. Jour. Amer. Chem. Soc. 39 1133 (1917).
2. Jour. Amer. Chem. Soc. 42 496 (1920).
3. Jour. Amer. Chem. Soc. 39 2534 (1917).
4. Jour. Amer. Chem. Soc. 31 390 (1909).
5. Jour. Amer. Chem. Soc. 38 1988 (1916).
6. Jour. Amer. Chem. Soc. 41 1086 (1919).

A STUDY OF LIQUID JUNCTION  
POTENTIALS

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C O N T E N T S

	Page
1. Introduction - - - - -	1
2. The Evaluation of Liquid Potential - - - - -	5
3. Experimental Procedure (a) Choice of Electrodes - - -	22
(b) Development of the Liquid Junction Apparatus - - - - -	29
(c) Manipulation - - - - -	33
4. Preparation of Material - - - - -	44
5. Experimental Results - - - - -	45
6. The Activities of the Chloride Ions in Sodium Chloride and in Lithium Chloride Solutions - - - - -	53

# A STUDY OF LIQUID JUNCTION POTENTIALS.

## 1. INTRODUCTION.

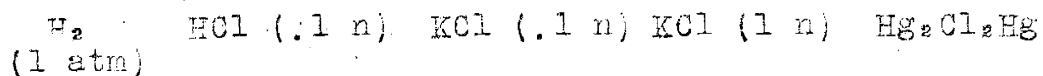
When two solutions of different electrolytes or of the same electrolyte but of different concentrations meet together at a junction, it gives rise to an electromotive force at the junction. The causes of this electromotive force will be treated in more detail presently. Different investigators designate this electromotive force with different names, but they all mean the same thing. A. A. Noyes calls it "liquid potential"; D. A. MacInnes calls it "liquid junction potential"; M. Planck calls it "potential between solutions"; and P. Henderson calls it "liquid cell potential." Following the usage of this laboratory we shall call it liquid potential.

In general there are three types of liquid junctions, namely two solutions of the same electrolyte but of different concentrations, e.g. NaCl .1 n NaCl .01 n, two solutions of different

electrolytes with a common ion but of the same concentration, e.g. NaCl .1 n KCl .1 n, and lastly two solutions of any electrolytes and of any concentration e.g. KNO<sub>3</sub> .1 n NaCl .01 n.

Liquid potentials have been one of the greatest stumbling blocks in electromotive force measurement involving fundamental principles. Their importance is well illustrated in the case of the establishing of a standard half-cell whose electrode potential we can arbitrarily assume to be zero. Three half-cells have been proposed to be called standard, namely Hg Hg<sub>2</sub>Cl<sub>2</sub> KCl (1 n); H<sub>2</sub> (1 atm) H<sup>+</sup>(1 m); and H<sub>2</sub> (1 atm) H<sub>2</sub>SO<sub>4</sub> .2n. The calomel electrode has certain experimental advantages over the others, because it is constant and reproducible, as was found by Sauer.<sup>1</sup> The molal hydrogen electrode H<sub>2</sub> (1 atm) H<sup>+</sup> (1 m) has the simplest theoretical significance. The half-cell H<sub>2</sub> (1 atm) H<sub>2</sub>SO<sub>4</sub> .2n is really unsuitable for standard electrode, because of complication produced by the presence of polyvalent ions. The choice is between the first two. It is still an open question whether the calomel electrode, or the molal hydrogen electrode should be adopted as the standard electrode. Whatever may our individual preference be, we can calculate any

specific electrode potential referring to one standard from that referring to the other, if we know the difference between the calomel electrode potential and the molal hydrogen electrode potential. In order to find the difference between these electrode potentials we have to measure a cell of this type



Suppose the value measured is  $E$ . Assuming the value of  $\text{Hg} \text{Hg}_2\text{Cl}_2 \text{KCl} 1 \text{ n}$  to be zero,  $E$  is the resultant of the three values  $E_{\text{H}_2 \text{HCl} .1 \text{ n}}$ ,  $E_{\text{HCl} .1 \text{ n}, \text{KCl} .1 \text{ n}}$  and  $E_{\text{KCl} .1 \text{ n}, \text{KCl} 1 \text{ n}}$ . If one can find some way to ascertain the values of  $E_{\text{HCl} .1 \text{ n}, \text{KCl} .1 \text{ n}}$  and  $E_{\text{KCl} .1 \text{ n}, \text{KCl} 1 \text{ n}}$ , then we can calculate the values of  $E_{\text{H}_2 (1 \text{ atm}) \text{HCl} .1 \text{ n}}$  by subtraction

$$\begin{aligned} E_{\text{H}_2 (1 \text{ atm}) \text{HCl} .1 \text{ n}} &= E - E_{\text{HCl} .1 \text{ n}, \text{KCl} .1 \text{ n}} \\ &\quad - E_{\text{KCl} .1 \text{ n}, \text{KCl} 1 \text{ n}}. \end{aligned}$$

Having found the value of  $E_{\text{H}_2 (1 \text{ atm}) \text{HCl} .1 \text{ n}}$ , from the activity of  $\text{H}^+$  in  $.1 \text{ n HCl}$  one can calculate the value of molal hydrogen electrode

$$\bar{E}_{\text{H}_2 (1 \text{ atm}) \text{H}^+ 1 \text{ m}} = E_{\text{H}_2 (1 \text{ atm}) \text{HCl} .1 \text{ n}} + \frac{RT}{F} \ln A_{\text{H}^+ .1 \text{ n}}$$

It is, however, not easy to determine the values of liquid potentials. They evade direct observation, complete elimination, or rigorous calculation and they are always sources of experimental uncertainty.

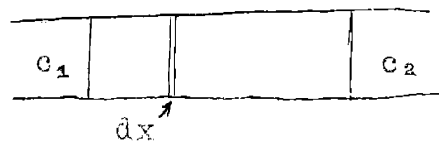
Thus in our case of determining the molal hydrogen electrode potential, as long as there is uncertainty in our liquid potentials  $E_{\text{HCl } .1 \text{ n KCl } .1 \text{ n}}$  and  $E_{\text{KCl } .1 \text{ n KCl } 1 \text{ n}}$ , there will always be an uncertainty in our molal hydrogen electrode potential. As many problems of similar importance involve the determination of liquid potentials, so a systematic study of the subject is of real importance. Important as this field of investigation is, a review of chemical literature shows that though this problem of liquid potential has been treated by men of international reputation, their attention has been directed to purely theoretical speculation, and no experimental work of any high degree of accuracy has been carried out. It is the object of this research to determine accurately the liquid potentials of various chlorides of the alkali elements and to interpret the results in the light of modern ionic theory.

## 2. THE EVALUATION OF LIQUID POTENTIAL.

Hernst<sup>2,3</sup> was the first investigator who attempted to formulate equations to calculate liquid potential. In spite of several inexact assumptions in the derivation, he was the first to explain the causes of liquid potential. Hernst postulated that when an electrolyte is diffusing across a boundary the ions are subjected to two kinds of force: osmotic and electrostatic. He considered the type of liquid potential of two solutions of the same electrolyte and of two different concentrations e.g. HCl ( $c_1$ ) HCl ( $c_2$ ). On the same postulate Planck derived a general equation for all types of liquid potential. His first doubtful assumption is that the electrolyte is completely dissociated, so that the undissociated molecules of HCl may be disregarded. This assumption, apparently unjustifiable, has been supported by physical and chemical evidences, recently pointed out by Professor A. A. Noyes and Professor D. A. MacInnes<sup>4</sup> of this laboratory, Ghosh<sup>5</sup> of India, Miller<sup>6</sup> of England and Bjerrum<sup>7</sup> of Germany.



Then on the positively charged hydrogen ion and on the negatively charged chlorine ion, there will be exerted the same force due to the gradient of the osmotic pressure. This will tend to move them from places of higher concentration to lower concentration. But from evidences of conductivity we know that the hydrogen ions move faster than the chloride ions, thus a partial separation of the ions occurs. As a result of their charges, there will arise an electrostatic force. This will retard the H ions and accelerate the Cl ions. Then he proceeded to evaluate the osmotic force and the electrostatic force on the individual ions.



Suppose  $c_1 > c_2$

Let  $q =$  cross section

$dx =$  infinitesimal distance from  $c_1$

$p =$  osmotic pressure of the ions between  $c_1$  and  $c_1 + dc$

$E =$  electrostatic force per mol ion

$U =$  mobility of cation

$V =$  mobility of anion

$t =$  time.

Then the quantity of cation and anion, which will migrate through the cross section  $q$ , in time  $dt$ , if acted upon by the osmotic force alone, will be equal to the product

$$(q)(c)\left(\frac{1}{c} \frac{dp}{dx}\right)(U)(dt)$$

$$(q)(c)\left(\frac{1}{c} \frac{dp}{dx}\right)(V)(dt)$$

The quantity of cation and anion migrating through the cross section  $q$  in time  $dt$  if acted upon by electrostatic force alone will be

$$(q)(c)F\left(\frac{dE}{dx}\right)(U)(dt)$$

$$- (q)(c)F\left(\frac{dE}{dx}\right)(V)(dt).$$

As a matter of fact these two forces act together and there are as many cations as anions that cross the boundary, we obtain the following equation

$$U q dt \left( \frac{dp}{dx} + cF \frac{dE}{dx} \right) = V q dt \left( \frac{dp}{dx} - cF \frac{dE}{dx} \right)$$

$$F \frac{dE}{dx} = - \frac{U - V}{U + V} \frac{1}{c} \frac{dp}{dx}$$

By assuming that the solute obeys the perfect solution law

$$p = c R T$$

$$F \frac{dE}{dx} = - \frac{U - V}{U + V} RT \frac{dc}{dx}$$

With the further assumption that the mobilities of the ions are independent of the concentration, **by**

integration the above equation between  $c_1$  and  $c_2$  gives

$$\begin{aligned} F \int_{E_1}^{E_2} \frac{dE}{U+V} &= F(E_2 - E_1) = - \frac{U-V}{U+V} RT \int_{c_1}^{c_2} \frac{dc}{c} \\ &= - \frac{U-V}{U+V} RT \ln \frac{c_2}{c_1} \\ &= \frac{U-V}{U+V} RT \ln \frac{c_1}{c_2} \end{aligned}$$

My investigation on liquid potential is not of the type to which this formula is applicable, but the fact that later Planck used the same assumptions in regard to complete ionization and mobility independent of concentration, and Planck believed the same forces, osmotic and electrostatic, acting on the ion, might justify a comprehensive discussion of Nernst derivation. Recently Professor D. A. MacInnes<sup>8</sup> has derived a new equation for liquid potential of the same type thermodynamically and free from the above assumptions.

$$E_L = E_t \left( 1 - \frac{1}{2 N_c} \right)$$

where  $E_L$  = liquid potential

$E_t$  = e.m.f. of cell with transference

$N_c$  = transference number of the cation.

In the above formulae both Nernst and MacInnes assumed that the activities of the cation and the anion are equal. Recently evidences have been point-

ed out by MacInnes<sup>9</sup> that they are not necessary. With this idea in view a new formula is developed by considering the free energy decrease attending the transference of individual ions across the boundary. Let us consider the liquid potential of



when one faraday of electricity has passed through the junction,  $T_H H^+$  is transferred from ( $c_1$ ) to ( $c_2$ ) and  $T_{Cl} Cl^-$  is transferred from ( $c_2$ ) to ( $c_1$ ). The free energy decrease accompanying the change of state is

$$-\Delta F = T_H RT \ln \frac{A_{H^+}(c_1)}{A_{H^+}(c_2)} + T_{Cl} RT \ln \frac{A_{Cl^-}(c_2)}{A_{Cl^-}(c_1)}$$

F = free energy

$T_H$  = transference number of  $H^+$

R = gas constant

T = absolute temperature

A = activity.

$$-\Delta F = T_H RT \ln \frac{A_{H^+}(c_1)}{A_{H^+}(c_2)} + (1 - T_H) RT \ln \frac{A_{Cl}(c_2)}{A_{Cl}(c_1)}$$

$$= T_H RT \ln \frac{A_H(c_1)}{A_H(c_2)} + T_H RT \ln \frac{A_{Cl}(c_1)}{A_{Cl}(c_2)}$$

$$+ RT \ln \frac{A_{Cl}(c_2)}{A_{Cl}(c_1)}$$

$$= T_H RT \ln \frac{A_H(c_1) A_{Cl}(c_1)}{A_H(c_2) A_{Cl}(c_2)} + RT \ln \frac{A_{Cl}(c_2)}{A_{Cl}(c_1)}$$

$$E_L = T_H \frac{RT}{F} \ln \frac{A_H(c_1) A_{Cl}(c_1)}{A_H(c_2) A_{Cl}(c_2)} + \frac{RT}{F} \ln \frac{A_{Cl}(c_2)}{A_{Cl}(c_1)}$$

As soon as the activities of the individual ions at all concentration have been measured, which I hope to do in the near future, this formula can be put to use. Its derivation is free from the objectionable assumptions of Nernst and it takes into consideration the difference in the activity of the cation and anion.

After Nernst there are no less than six equations advanced to calculate liquid potentials of various types. But the ones that deserve careful attention are those of Planck and Henderson. The rest will be only mentioned.

Planck<sup>10</sup> considered the most general case of any number of binary electrolytes of any concentrations on each side, being dilute enough to dissociate completely. Whatever objections have been raised against Nernst's assumptions can also be raised against Planck's. As it has been demonstrated, the number of cations and anions passing through the boundary acted upon by osmotic and electrostatic forces are

$$u \quad q \quad dt \quad \left( \frac{dp}{dx} + cF \frac{dE}{dx} \right) \quad c = \text{conc. cations}$$

$$v \quad q \quad dt \quad \left( \frac{dp}{dx} - \bar{c}F \frac{dE}{dx} \right) \quad \bar{c} = \text{conc. anions}$$

or for unit time and unit cross section, and expressing  $p$  in terms of  $c$

$$dc = u \left( RT \frac{dc}{dx} + cF \frac{dE}{dx} \right)$$

$$d\bar{c} = v \left( RT \frac{d\bar{c}}{dx} - \bar{c}F \frac{dE}{dx} \right)$$

Planck went one step further and considered the case in which the concentration gradient  $\frac{dc}{dx}$  is not uniform, so he differentiated the expressions again and obtained

$$\frac{\partial c}{\partial t} = u \left( RT \frac{\partial^2 c}{\partial x^2} \right) + u F \frac{\partial}{\partial x} \left( c \frac{\partial E}{\partial x} \right)$$

$$\frac{\partial \bar{c}}{\partial t} = v RT \frac{\partial^2 \bar{c}}{\partial x^2} - v F \frac{\partial}{\partial x} \left( \bar{c} \frac{\partial E}{\partial x} \right)$$

Then if a stable condition is maintained

$$\frac{\partial c}{\partial t} = 0 \quad \frac{\partial \bar{c}}{\partial t} = 0$$

$$RT \frac{\partial^2 c}{\partial x^2} + F \frac{\partial}{\partial x} \left( c \frac{\partial E}{\partial x} \right) = 0$$

$$RT \frac{\partial^2 \bar{c}}{\partial x^2} - F \frac{\partial}{\partial x} \left( \bar{c} \frac{\partial E}{\partial x} \right) = 0$$

Integrating  $A = RT \frac{\partial c}{\partial x} + F c \frac{\partial E}{\partial x}$  A = integration constant (1)

$$B = RT \frac{\partial \bar{c}}{\partial x} - F \bar{c} \frac{\partial E}{\partial x} \quad (2)$$

Then he considers that the boundary layer is of finite thickness . As  $x$  changes from 0 to  $\delta$  , - the concentration changes from that of one side  $c_1$  to that of the other  $c_2$

$$A + B = 2 RT \frac{dc}{dx}$$

Integrating  $(A + B) x + \text{const.} = 2 RT c$

To express  $c$  in terms of  $c_1$  and  $c_2$

$$\text{when } x = 0 \quad c = c_1$$

$$2 RT c_1 = \text{const.}$$

$$c_1 = \frac{\text{const.}}{2 RT}$$

$$\text{when } x = \delta \quad c = c_2$$

$$2 RT c_2 = (A + B)\delta + \text{const.}$$

$$2 RT (c_2 - c_1) = (A + B)\delta \quad \frac{A+B}{2 RT} = \frac{c_2 - c_1}{\delta}$$

$$c = \frac{A + B}{2 RT} x + \frac{\text{const.}}{2 RT} = \left( \frac{c_2 - c_1}{\delta} \right) x + c_1 \quad (3)$$

Now subtracting (2) from (1) and substituting  $c$  from equation (3) we obtain

$$A - B = 2 F c \frac{\partial E}{\partial x} = 2 F \left[ \frac{c_2 - c_1}{\delta} x + c_1 \right] \frac{\partial E}{\partial x}$$

$$\therefore \frac{\partial E}{\partial x} = \frac{(A - B) \delta}{2 F [(c_2 - c_1)x + c_1 \delta]}$$

Integrating between the limit of 0 to  $\delta$  for  $x$

$$E_2 - E_1 = \frac{(A - B) \delta}{2 F (c_2 - c_1)} \ln \frac{c_2}{c_1}$$

For the sake of brevity let  $\xi = \left( \frac{c_2}{c_1} \right)^{\frac{(A-B)\delta}{2RT(c_2-c_1)}}$

$$\therefore E_2 - E_1 = \frac{RT}{F} \ln \xi$$

Now it remains to eliminate the constants A and B.

To do this let

$$u c = \bar{U} \quad \text{and} \quad v \bar{c} = \bar{V}$$

$$D = u A = RT \frac{\partial \bar{U}}{\partial x} + F \bar{U} \frac{\partial E}{\partial x} = RT \frac{\partial \bar{U}}{\partial x}$$

$$D = v B = RT \frac{\partial \bar{V}}{\partial x} - F \bar{V} \frac{\partial E}{\partial x} = RT \frac{\partial \bar{V}}{\partial x} - \bar{V} \frac{(A-B)\delta}{2[(c_2-c_1)x + c_1\delta]}$$

By integrating these differential equations of the first order, the first equation gives

$$\bar{U} = \frac{2 D [(c_2-c_1)x + c_1\delta]}{2 (c_2-c_1) RT + (A-B)\delta} + [(c_2-c_1)x + c_1\delta]^{\frac{(A-B)\delta}{2(c_2-c_1)RT}} + \text{Const.}$$

$$\text{when } x = 0 \quad \bar{U} = \bar{U}_1$$

$$x = \quad \bar{U} = \bar{U}_2$$

With two equations, the integration constant can be eliminated. With the introduction of  $\xi$  we have

$$\xi \bar{U}_2 - \bar{U}_1 = \frac{2 D \delta (\xi c_2 - c_1)}{2 (c_2 - c_1) RT + (A-B) \delta}$$

Similarly

$$\bar{V}_2 - \xi \bar{V}_1 = \frac{2 D \delta (c_2 - \xi c_1)}{2 (c_2 - c_1) RT - (A-B) \delta}$$

$$\ln \xi = \frac{(A-B)\delta}{2 (c_2 - c_1) RT} \ln \frac{c_2}{c_1}$$

$$(A-B)\delta = \frac{2 (c_2 - c_1) RT \ln \xi}{\ln \frac{c_2}{c_1}}$$



$$\frac{\xi \bar{U}_2 - \bar{U}_1}{v_2 - \xi v_1} = \frac{2(c_2 - c_1) RT - (A-B) \delta}{2(c_2 - c_1) RT + (A-B) \delta} \frac{\xi c_2 - c_1}{c_2 - \xi c_1}$$

$$= \frac{\ln \frac{c_2}{c_1} - \ln \xi}{\ln \frac{c_2}{c_1} + \ln \xi} \cdot \frac{\xi c_2 - c_1}{c_2 - \xi c_1}$$

Thus  $\xi$  is completely defined by terms, the data of which are readily available.

If  $u_2 = u_1$  (the mobilities independent of concentration, which cannot be true) then

$$\frac{u}{v} = \frac{\ln \frac{c_2}{c_1} - \ln \xi}{\ln \frac{c_2}{c_1} + \ln \xi}$$

$$\ln \xi = \ln \frac{c_2}{c_1} \left( \frac{v - u}{u + v} \right)$$

which is the same as the Nernst equation.

If  $c_2 = c_1$  as in the case HCl .1 n KCl .1 n

Then

$$\xi = \frac{v_2 + u_1}{u_2 + v_1}$$

$$E = \frac{RT}{F} \ln \frac{v_2 + u_1}{u_2 + v_1}$$

Here the anion is common

$$E = \frac{RT}{F} \ln \frac{u_1 + v_1}{u_2 + v_2} = \frac{RT}{F} \ln \frac{\Lambda_{\text{H}}^+ + \Lambda_{\text{Cl}}}{\Lambda_{\text{K}} + \Lambda_{\text{Cl}}}$$

for mobilities are proportional to equivalent conductance. Since Planck assumed complete ionization the  $\Lambda$  to correspond to that condition is necessarily the  $\Lambda$  at infinite dilution. Lewis and Sargeant empiracally found that experiments agreed with their modified formula better.

$$E = \frac{RT}{F} \ln \frac{\Lambda_1}{\Lambda_2}$$

However, inasmuch as their method of making the liquid junction was crude, we cannot help but be more or less dubious.

Through a very different line of reasoning Henderson<sup>12</sup> derived the following equation.

$$E = \frac{RT}{F} \frac{(\bar{U}_1 - \bar{V}_1) - (\bar{U}_2 - \bar{V}_2)}{(\bar{U}_1 + \bar{V}_1) - (\bar{U}_2 + \bar{V}_2)} \ln \frac{\bar{U}_1 + \bar{V}_1}{\bar{U}_2 + \bar{V}_2}$$

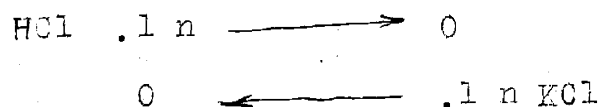
R, T, F have the usual meaning.

$\bar{U}$  =  $\sum cu$  or the summation of the products of concentration times mobility of the cations.

$\bar{V}$  =  $\sum cv$  or the summation of the products of concentration times the mobility of the anions.

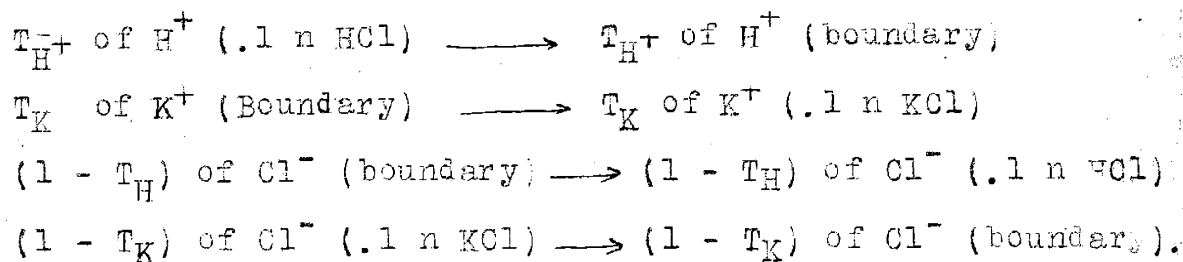
In a very similar way, though independent of Henderson, I derived the following formula for the simple case of two binary electrolytes with common anion and of same concentration, with the aid of a few suggestions found in Noyes & Sherrill's "General Principles of Chemistry" page 166.

Let us consider the junction between .1 normal HCl and .1 normal KCl



The concentration of HCl decreases from .1 normal to zero from left to right, and the concentration of KCl increases from zero to .1 normal in the same direction, when one faraday of electricity passes through the

junction, the following changes take place,



Since there is as much  $Cl^-$  coming into the boundary as leaving and the  $Cl^-$  ions is constant<sup>30</sup> everywhere, we can neglect its transfer. The free energy decrease attending the transfer of the  $H^+$  and  $K^+$  is

$$-dF = T_H RT d \log \frac{C_H}{C_H - \Delta C_H} + T_K RT d \log \frac{C_K}{C_K + \Delta C_K}$$

We are now considering only a small portion of the boundary between  $C_H$  and  $C_H - \Delta C_H$ ,  $C_K$  and  $C_K + \Delta C_K$ .

In general mathematics

$$\log \frac{c}{c - \Delta c} = \log c - \log (c - \Delta c) = \log \int_{c-\Delta c}^c \frac{dc}{c}$$

$$\therefore -dF = T_H RT \frac{dC_H}{C_H} + T_K RT \frac{dC_K}{C_K}$$

$$T_H = \frac{C_H \Lambda_H}{C_H \Lambda_H + C_K \Lambda_K + C_{Cl} \Lambda_{Cl}}$$

$$T_K = \frac{C_K \Lambda_K}{C_H \Lambda_H + C_K \Lambda_K + C_{Cl} \Lambda_{Cl}}$$

$$\begin{aligned}
 -\Delta F &= RT \int_0^{.1\alpha} T_H \frac{dC_H}{C_H} + RT \int_0^{.1\alpha} T_K \frac{dC_K}{C_K} \\
 &= RT \int_0^{.1\alpha} \frac{C_H \Lambda_H dC_H}{(C_H \Lambda_H + C_K \Lambda_K + C_{Cl} \Lambda_{Cl}) C_H} + RT \int_0^{.1\alpha} \frac{C_K \Lambda_K dC_K}{(C_H \Lambda_H + C_K \Lambda_K + C_{Cl} \Lambda_{Cl}) C_K}
 \end{aligned}$$

Assuming that the sum of the  $H^+$  and  $K^+$  at the boundary is equal to the  $Cl^-$ , then

$$\begin{aligned}
 c_H &= c_{Cl} - c_K \\
 c_K &= c_{Cl} - c_H \\
 -\Delta F &= RT \int_{.1\alpha}^0 \frac{\Lambda_H dc_H}{c_H \Lambda_H + c_{Cl} \Lambda_K - c_H \Lambda_K + c_{Cl} \Lambda_{Cl}} \\
 &+ RT \int_0^{.1\alpha} \frac{\Lambda_K dc_K}{c_{Cl} \Lambda_H - c_K \Lambda_H + c_K \Lambda_K + c_{Cl} \Lambda_{Cl}} = \\
 &RT \int_{.1\alpha}^0 \frac{\Lambda_H dc_H}{c_H (\Lambda_H + \Lambda_K) + c_{Cl} (\Lambda_K + \Lambda_{Cl})} \\
 &+ RT \int_0^{.1\alpha} \frac{\Lambda_K dc_K}{c_K (\Lambda_K - \Lambda_H) + c_{Cl} (\Lambda_H + \Lambda_{Cl})}
 \end{aligned}$$

Performing the integration,

$$\begin{aligned}
 -\Delta F &= \frac{RT \Lambda_H}{\Lambda_H - \Lambda_K} \ln \left\{ c_H (\Lambda_H - \Lambda_K) + c_{Cl} (\Lambda_K + \Lambda_{Cl}) \right\} \Big|_{.1\alpha}^0 \\
 &+ \frac{RT \Lambda_K}{\Lambda_K - \Lambda_H} \ln \left\{ c_K (\Lambda_K - \Lambda_H) + c_{Cl} (\Lambda_H + \Lambda_{Cl}) \right\} \Big|_0^{.1\alpha} \\
 &= \frac{RT \Lambda_H}{\Lambda_H - \Lambda_K} \ln \frac{c_{Cl} (\Lambda_K + \Lambda_{Cl})}{.1\alpha (\Lambda_H - \Lambda_K) + c_{Cl} (\Lambda_K + \Lambda_{Cl})} \\
 &+ \frac{RT \Lambda_K}{\Lambda_K - \Lambda_H} \ln \frac{.1\alpha (\Lambda_K - \Lambda_H) + c_{Cl} (\Lambda_H + \Lambda_{Cl})}{c_{Cl} (\Lambda_H + \Lambda_{Cl})}
 \end{aligned}$$

According to the foregoing assumption

$$\begin{aligned}
 c_{Cl} &= .1\alpha \\
 \text{Then } -\Delta F &= \frac{RT \Lambda_H}{\Lambda_H - \Lambda_K} \ln \frac{\Lambda_K + \Lambda_{Cl}}{\Lambda_H + \Lambda_{Cl}} + \frac{RT \Lambda_K}{\Lambda_K - \Lambda_H} \ln \frac{\Lambda_K + \Lambda_{Cl}}{\Lambda_H + \Lambda_{Cl}} \\
 &= \frac{RT (\Lambda_H - \Lambda_K)}{\Lambda_H - \Lambda_K} \ln \frac{\Lambda_K + \Lambda_{Cl}}{\Lambda_H + \Lambda_{Cl}} = RT \ln \frac{\Lambda_K + \Lambda_{Cl}}{\Lambda_H + \Lambda_{Cl}}
 \end{aligned}$$

There are two objections to this derivation. First of all, while the electrical force pulls the potassium ion from the boundary to the .1 normal KCl, the osmotic force will tend to pull it from the .1 normal KCl to the boundary. How much does this tendency of a salt to go from places of higher concentration to low concentration effect our free energy decrease in the transference of ions, we do not know. Secondly, the following equation cannot be true

$$C_H + C_K = C_{Cl}$$

While the ion constituents of H and K are equal to that of Cl at the boundary, the sum of the effective concentrations of  $H^+$  and  $K^+$  is by no means equal to that of  $Cl^-$ . We are still uncertain about the values of the activities of the individual ions, <sup>but</sup> we know qualitatively that the activity of the  $H^+$  is greater than that of  $K^+$ , since the activity of HCl at .1 normal is greater than that of KCl at the same concentration, and the activities of the  $Cl^-$  are the same in both cases. Unfortunately there exists insufficient data to make quantitative correction in the present derivation.

12a

J. M. Loven considered the case where the anions are common and the cations are bivalent and univalent e.g. HCl, BaCl<sub>2</sub>.

The conclusion is

$$E_L = .0002 T \frac{3u_1 - 2u_2 + v}{3u_1 - 4u_2 - v} \ln \frac{3(u_1 + v)}{4(u_2 + v)}$$

in which

$u_1$  = migration velocity of the univalent cation

$u_2$  = " " " " bivalent "

$v$  = " " " " anion.

The formula was tested by experiment and found that it agrees fairly well at very dilute solutions and not very well even at moderate concentration.

Following Nernst's and Planck's method of treatment K. R. Johnson<sup>13</sup> derived the following equation for polyvalent cations and anions:

$$\frac{\bar{U}_2 e^{\frac{p F E}{R}} - \bar{U}_1}{\bar{V}_2 - \bar{V}_1 e^{\frac{q F E}{R}}} = \frac{q}{p} \frac{\ln \left( \frac{C_2}{C_1} \right) - \frac{q F E}{R}}{\ln \left( \frac{C_2}{C_1} \right) + \frac{p F E}{R}} \frac{\frac{C_2}{C_1} e^{\frac{p F E}{R}} - 1}{\frac{C_2}{C_1} - e^{\frac{q F E}{R}}}$$

$q$  = valence of cation

$p$  = " " anion.

Other symbols have the same significance as those in the Planck equation.

J. Guyot<sup>14</sup> has published a paper summarizing the work done by Nernst, Planck, Loven and Johnson.

In order to avoid the objection of complete ionization, Melander<sup>15</sup> took into consideration the undissociated molecules and considered them to be only acted upon by the osmotic force and not by the

electric force. But he made another assumption which is worse than that of complete ionization, that is, the strong electrolytes obey the mass action law. For the case of two electrolytes with a common anion his equation is

$$E = - \frac{R}{F} \left\{ \frac{\left[ \frac{a_1}{a_3} \left( \frac{a_4^2}{2a_3} - a_2 + a_4 a_5 \right) - a_2 \right] \ln \left[ \bar{C}_2 - \frac{a_4}{2a_3} - a_5 \right]}{2 a_5 \left( \frac{a_4}{2a_3} + a_5 \right) (\bar{C}_1 - \frac{a_4}{2a_3} - a_5)} \right\} +$$

$$\frac{R}{F} \left[ \frac{\frac{a_1}{a_3} \left( \frac{a_4^2}{2a_3} - a_2 + a_4 a_5 \right) - a_2}{2 a_5 \left( \frac{a_4}{2a_3} - a_5 \right) (\bar{C}_1 - \frac{a_4}{2a_3} + a_5)} \right] \ln \left[ \bar{C}_2 - \frac{a_4}{2a_3} + a_5 \right] - a_3 \ln \frac{\bar{C}_2}{C_1}$$

$$a_1 = (\alpha^1 - \frac{\alpha \gamma}{K'K''}) \quad a_2 = k(u' - u'') \quad a_3 = (\alpha^1 + \frac{\alpha \gamma}{K'K''})$$

$$a_4 = 2(u' - u'') \quad a_5 = \sqrt{\frac{a_4^2}{4 a_3^2} - \frac{a_2}{a_3}}$$

$K'K''$  = ionization constants

$\alpha$  = ionization

$u$  = mobility of cation

$v$  = " " anion

It is so complicated that we can hardly realize the physical significance of each term.

<sup>16</sup>  
G. Gouy thought that the most practical treatment is upon the case where mixing has taken place and he derived the following equation for such a case

$$E = \frac{RT}{F} \frac{Y_1(u-v) - Y_2(u-v)}{Y_1(pu+pv) - Y_2(pu+pv)} \ln \frac{Y_1(pu+\bar{p}v)}{Y_2(pu+pv)}$$

$$Y_1 = p'c'_1 = \bar{p}'\bar{c}'_1$$

$p$  = valence

$c$  = concentration

Other symbols have the usual significance.

In the foregoing I have briefly described the six equations for the evaluation of liquid potentials. Each of them aimed to correct the wrong assumptions of the others, and in doing so other and sometimes unjustifiable assumptions were introduced. None seems to be perfectly satisfactory. The only solution of the problem lies in accurate experimental determination.

The investigations of W. Negbauer<sup>17</sup>, Nernst, and Pauli,<sup>18</sup> Tower<sup>19</sup> must be looked upon as a qualitative confirmation of Planck's theory, since their methods were so crude, and they attempted some very complicated cases with several junctions. They used calomel electrodes for even dilute solutions. Personal experience and experience of other investigators have shown that such electrodes give varying potentials.

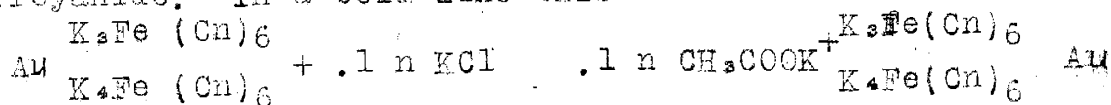


### 3. EXPERIMENTAL PROCEDURE

#### a. Choice of Electrodes.

In the measurements of any cell that involves liquid potential there are always three sources of electromotive force, namely, the two electrodes and the liquid junction. If we can find two electrodes whose single potentials are the same, then the electromotive force of the cell measured is the liquid potential. Therefore the first step in any accurate liquid potential measurement is the choice of two reversible electrodes whose potentials are equal.

The first choice fell on the ferro-ferricyanide electrode recommended by Lewis and Sargent<sup>20</sup> who claimed them to be reproducible to .0001 volt. The electrode consisted of a gold spiral dipped into a solution of some electrolyte, say KCl, containing a definite amount of stock solution of ferrocyanide and ferricyanide. In a cell like this



if the quantities of  $\text{K}_3\text{Fe}(\text{Cn})_6$   $\text{K}_4\text{Fe}(\text{Cn})_6$  were the same at both electrodes, and if the influence of KCl and  $\text{CH}_3\text{COOK}$  on the ionization of  $\text{K}_3\text{Fe}(\text{Cn})_6$ ,  $\text{K}_4\text{Fe}(\text{Cn})_6$  were the same, then we had a simple way of measuring the

liquid potential. I first wanted to ascertain to what degree ~~were~~ the ferro-ferricyanide electrodes reversible. About .5 cc. of .5 n  $K_3Fe(CN)_6$  solution and .5 cc. of .5 n  $K_4Fe(CN)_6$  solution were added to 100 cc. of .1 n KCl solution. Four clean gold electrodes were dipped into that solution. If they were strictly reversible, they ought to give zero potential while they actually measured

a - b	.00210
a - c	.00293
a - d	.00123

By electroplating the gold electrodes in a gilding bath, I hoped to improve their reversibility. The gilding bath was made by dissolving 1.4 gram of Au in aqua regia, driving off the excessive acid, precipitating the Au with KCN, filtering and washing the  $Au(CN)_3$ , redissolving it in KCN<sup>N</sup> and finally diluting it to 200 cc. A current of .003 amp. was used for each electrode of 4 cm. in length and 3 mm in diameter. After the electrolysis the electrodes were washed and dipped into the ferro-ferricyanide solution as before. They measured respectively

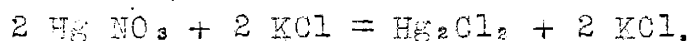
a - b	.00031
a - c	-.00115
a - d	-.00090

There was a decided improvement, but they were still not good enough. As further electroplating gave no better result, they had to be abandoned.

a - b            -.00124  
a - c            .00138  
a - d            -.00424

Calomel electrodes (1, 21, 20, 22, 23) were tried next. In order to make pure calomel, I had to start with pure mercury. To purify the mercury I covered the mercury with a dilute solution of  $\text{HNO}_3$  and let air bubble through the mercury for twenty-four hours so that the more basic metallic impurities would be oxidized and dissolved by the  $\text{HNO}_3$ . Then the mercury is dried by letting it go through a capillary. It was finally redistilled twice under reduced pressure.

Mercurous nitrate was prepared by digesting the purified Hg with cold moderately concentrated  $\text{HNO}_3$ , keeping an excess of Hg present all the time. By adding dilute KCl to dilute  $\text{HgNO}_3$  solution, calomel was precipitated



It has been found by Sauer<sup>1</sup> and Lewis<sup>20</sup> that the potential of the calomel electrode depends upon

the size of the  $\text{Hg}_2\text{Cl}_2$  particles. The reason may probably be due to the enormous surface of the colloidal particles on which the electrolyte is adsorbed, thus changing the concentration of the solution. In order to eliminate these fine particles the  $\text{Hg}_2\text{Cl}_2$  is decanted from 5 to 10 times, with the solution KCl or HCl as the case may be.

The  $\text{Hg}_2\text{Cl}_2$  is oxidizable by the air. To prevent this possible danger the  $\text{Hg}_2\text{Cl}_2$  was shaken with Hg and the solution with which the  $\text{Hg}_2\text{Cl}_2$  was intended to be used, for three days, until the white  $\text{Hg}_2\text{Cl}_2$  particles turned grey, being intimately mixed with the small globules of Hg. At the same time it also accomplished the purpose of bringing the  $\text{Hg}_2\text{Cl}_2$  into equilibrium with the solution. Five electrodes Hg  $\text{Hg}_2\text{Cl}_2$  .1 n KCl, were prepared and after standing in the thermostat for several hours at  $25^\circ\text{C}$ , they measured

a - b	+ .00007
a - c	- .00007
a - d	.00000
a - e	- .00006

The agreement was very gratifying. But the electrodes Hg  $\text{Hg}_2\text{Cl}_2$  .1 n HCl, prepared under identical

conditions, were so far apart that they were not acceptable

a - b	-.00106
a - c	-.00053
a - d	-.00044
a - e	-.00024

They not only disagreed but they also changed with the time, as also found by Sauer,<sup>1</sup> Meyer and Acree.<sup>21</sup> The latter measured the following cell



The following is a representative series of results.

28.10
27.91
27.69
28.19
27.61
27.61
27.66
27.56
27.61
<u>27.80</u>

27.77 Average.

The variation of more than half millivolt is due to electrode potential according to the investigators. They attributed it to the corrosive power of the HCl on the rubber stopper. The impurities of the rubber may be partly responsible for it, but another more plausible theory is that

the hydrogen ion has a great peptizing power on the  $\text{Hg}_2\text{Cl}_2$ . As the  $\text{Hg}_2\text{Cl}_2$  is peptized, the natural consequence is that the larger particles become colloidal. At one electrode the  $\text{Hg}_2\text{Cl}_2$  may be more peptized than at another electrode and therefore the potential of one electrode is higher than the other. The theory that the  $\text{H}^+$  ion might promote oxidation of  $\text{Hg}_2\text{Cl}_2$  by air, more than the  $\text{K}^+$  ion is rather hypothetical.

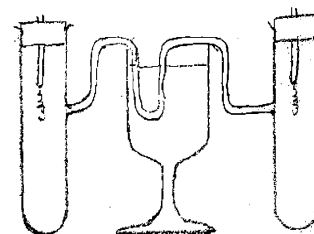
Silver, silver chloride electrodes made according to the description of MacInnes and Parker were tested and found to be extremely reversible, both in  $\text{KCl}$  and  $\text{HCl}$  solutions. The electrode consisted of a platinum gauze of one square centimeter. It was silver plated in a  $\text{K Ag}(\text{CN})_2$  bath at the current density of .003 amp. per sq. cm. Then it was immersed in distilled water, with frequent renewal of water, for twenty-four hours, before it was covered with silver chloride electrolytically at a current density of .007 amperes per sq. cm. in a bath of the solution at the same concentration in which the electrode was intended to be used. Thus six electrodes were prepared in .1 n  $\text{HCl}$  and they measured

		a-b	a-c	a-d	a-e	a-f
March 6	11:25	.005 mv.	.005	.070	.063	.053
	12:05	.010	.042	.065	.063	.032
	4:17	.000	.050	.037	.059	.037
March 7	8:55	-.018	.067	.051	.063	.102
	2:55	-.051	.129	.089	.104	-.037

In regard to mutual agreement and constancy with time the silver, silver chloride electrode is much better than the calomel electrode in HCl solution and far superior to the ferro-ferricyanide electrode. The above figures do show some variation, but they do not go beyond the range of my experiment. Besides that, out of the six electrodes we can easily pick three or four that agree excellently for a reasonable period of time. Later improvements even show better agreement than the above figures. So the silver, silver chloride electrode was finally adopted.

## b. Development of the Liquid Junction Apparatus.

Having found the silver, silver chloride electrode reliable enough for the purpose, it left the liquid junction to be investigated. First the simplest type of junction was tried, as shown in the figure. While this junction worked perfectly well with solutions of the same electrolyte of different concentration,<sup>24</sup> it did not work well at all with solutions of this type .1 n HCl .1 n KCl. Sometimes it gives higher value and sometimes lower. The e.m.f. changed with time as also found by Cumming,<sup>25</sup> Chanoz,<sup>26</sup> and Bjerrum.<sup>27</sup> In other words, it is neither reproducible nor constant. By means of colored solutions one can actually observe that the boundary is not sharp. Every time the junction is made, the boundary assumes a different shape from the one before. Besides this, since on one side of the junction we have a finite quantity of HCl and on the other side we have zero concentration of HCl, *vice versa* with KCl, the concentration





gradient is infinite and the diffusion tendency is consequently infinite also. If we have 1% of HCl, and add it to 99% of KCl, and 1% of KCl to 99% HCl, then the liquid potential shows reasonable constancy, e. i. .2 mv. for 4 hours.

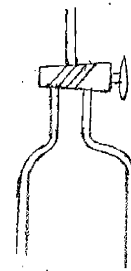
Ag AgCl(.099009 HCl + .00099009 KCl), (.099009 KCl + .00099009 HCl)  
 AgCl Ag

Time	e. m. f.	Time	e. m. f.
1:20	25.96	2:50	26.03
1:25	25.98	3:30	26.03
1:50	26.03	6:00	25.77
2:00	26.02		

This is why this type of junction is suitable for solutions of same electrolyte at different concentrations, but fails completely with solutions of different electrolytes of the same concentration. This is also why the older measurements of liquid potentials are unreliable, for this has been the common method employed.

The next type of junction tried was the ungreased ground glass stopcock of the shape shown.

It gave no satisfactory result. In fact the e. m. f. changed much faster with time than did the form of junction just described.



There are numerous other forms of liquid junction recommended by investigators. Bjerrum<sup>27</sup> used the sand junction. Cumming used the parchment paper separation. False and Vosburgh used an agar plug. None

of them is of much value. Either other investigator found that they are worthless or their own results showed themselves to be so. There is no need of trying them.

An intermittently flowing junction has been used by G. N. Lewis<sup>23</sup> and found satisfactory. The idea is to have a fresh surface of contact between the solution once a while.

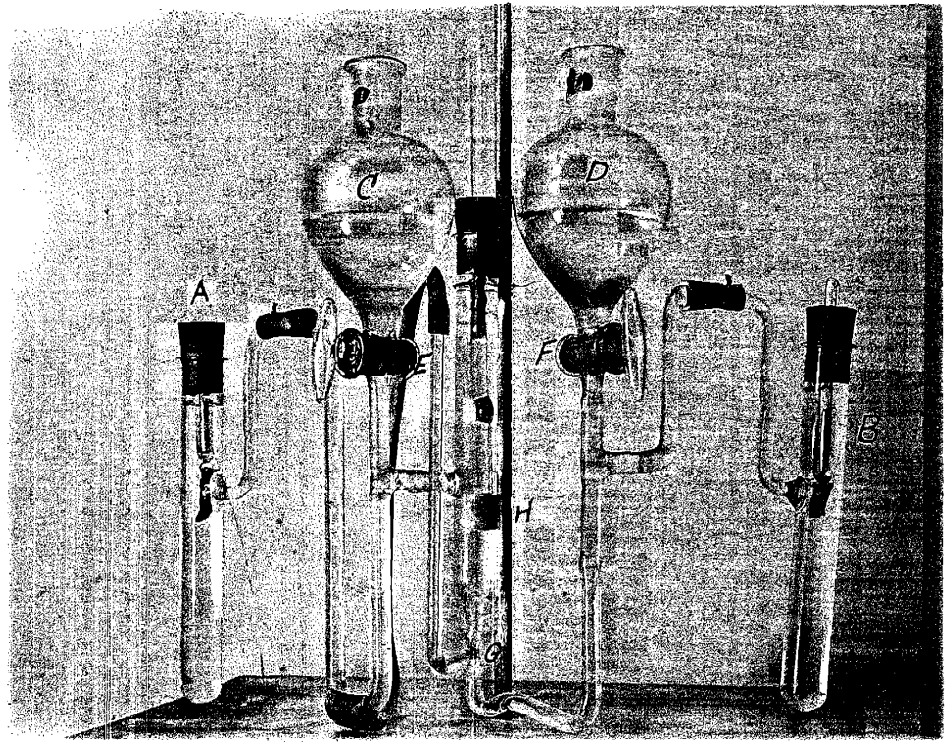
Since it is of advantage to have a fresh surface of contact between solutions once in a while, it should be so much better to have fresh contact all the time. This is the basis of the constantly flowing liquid junction. However I should not claim priority of this device, for the same idea was made use of by Lamb<sup>29</sup> and Larson of Harvard. It was said that it has been announced in an address in the American Academy of Arts and Sciences (1916) in a Harvard-Technology Club meeting, though I was not present.

The device is shown in the photographs. Figure 1 shows the general view of the whole apparatus. A and B are the parts containing the silver silver chloride electrodes, where the flow of the solutions does not disturb the equilibrium between the solutions and

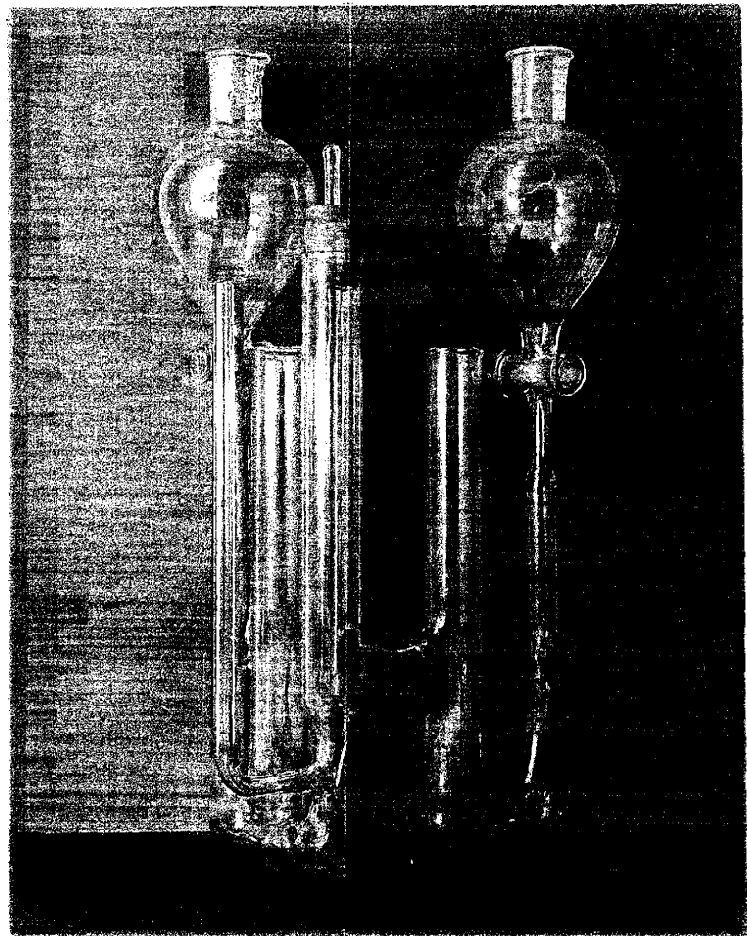
the electrodes. C and D are the reservoirs for the solutions, regulated by the stopcocks E and F. These stopcocks have holes specially enlarged, so that they will not entrap any air bubbles. If some air bubbles are entrapped below the stopcocks or if the holes are small there will always be some difference in the resistances to the flow, making the flow irregular. If the flow is irregular, it causes a difference in pressure heads on each side of the junction G, displacing the boundary to places other than G. That is detrimental to the liquid potential.

Attention is called to the indentation of the junction G. The indentation is necessary in order to get rid of the "dead space" where the mixed solutions stay more or less motionless. Without it we would have a boundary partly sharp and partly diffused. Thus we would not get the full benefit of the flow. The same effect was found by Lamb and Larson.

Another part of the apparatus which I found absolutely necessary but absent in the Lamb apparatus is the stopper H for the junction. It is for the purpose of preventing the mixing while the apparatus is being filled with solutions.



*Fig 1*



*Fig 2*

Figure 2 shows another apparatus for the same purpose of measuring liquid potential between dilute solutions. The electrodes are brought closer together and at the same time not disturbed by the current of the flow. The diameter of the tubes are much wider so as to reduce the electrical resistance. I found that for solutions .01 normal, the apparatus shown in Figure 2 gives more accurate potential measurements in the potentiometer than the apparatus represented in Figure 1

### c. Manipulation.

In liquid potential measurement careful manipulation is just as important as correct form of apparatus. Only through long experience and constantly correcting previous faults that one can find out its different precautions to take in the manipulation.

The main idea is to start the surface of contact between the solutions at G and maintain it at G throughout the measurement. If this is neglected no amount of flow will give reproducible results.

First of all the differences in pressure between the columns of solutions in the reservoirs will displace the junction. Sometimes by mixing the solutions, the pressure difference causes the composition of the entire solution to change. The liquid potential would be constant through several hours and yet the values would not be reproducible. In order to have equal pressure on both sides of the junction, one must have the surfaces of the solutions in the reservoirs at the same level, at the neck of the funnel. It is quite evident that if the level is at the neck of the funnel, even when the columns of solutions are not exactly at the same height, it takes only a small amount of liquid to go from one side to the other in order to equalize the pressure. On the other hand if the surfaces of the solutions are at the widest parts of the reservoirs, a slight difference in the heights of the columns will require a large volume of solution to flow from one side of the junction to the other in order to establish equal pressure, thus causing a hopeless uncertainty in the value of liquid potential.

As has been previously pointed out *in this* ~~and~~ *thesis* that the holes of the stopcocks of the res-

ervoirs must be sufficiently large in order to make their resistance to the flow negligible, otherwise their different resistance will cause irregular flow.

In filling the apparatus, the stopper H must be absolutely tight, not to allow any solution to go from one side of G to the other. If the solution happens to go to the other side of G it changes the composition of the second solution so uniformly that a false value is maintained for a long time. If that ever happens, it would be futile to go any further. The whole apparatus must be washed and dried again.

All the stopcocks are not to be opened (H last of all) until the apparatus is clamped in the thermostat which keeps the temperature  $\pm .01^{\circ}\text{C}$ . If the apparatus is tilted while the stopcocks are opened the junction will be displaced.

Generally the denser solution is at lower part of the junction and the lighter solution is above it, but several trials show that it makes no difference if the position is reversed.

Then there is the question of the rate of flow to be considered. Does it make any difference whether the rate be 1 drop a minute or 4 drops a minute or 10 drops a minute? This research shows that the rate has a decided influence. The electromotive

force of this cell:



was measured with different rates of flow at the junction with the results shown in Table I. The potentiometer was read at one minute intervals.

Table I

Time	Rate	e.m.f.	Time	Rate	e.m.f.
1:25	4 drops a min:	26.75 mv.	2:31	stop	26.94
2:00	"	26.78	2:32	"	26.94
2:01	stop	26.81	2:33	"	26.94
2:02	"	27.00	2:34	"	26.94
2:03	"	27.05	2:35	"	26.94
2:04	"	27.09	2:36	"	26.94
2:05	"	27.09	2:37	"	26.89
2:06	"	27.10	2:38	"	26.85
2:07	"	27.10	2:39	"	26.84
2:08	"	27.09	2:40	"	26.82
2:09	"	27.08	2:41	"	26.83
2:10	"	27.06	2:42	"	26.82
2:11	"	27.05	2:43	"	26.81
2:12	"	27.07	2:44	"	26.80
2:13	"	27.07	2:45	"	26.79
2:14	"	27.07	2:46	"	26.78
2:15	"	27.06	2:47	"	26.77
2:16	"	27.04	2:48	"	26.76
2:17	"	27.03	2:49	"	26.75
2:18	"	27.03	2:50	"	26.75
2:19	"	27.03	2:51	"	26.74
2:20	"	27.03	2:52	"	26.73
2:21	"	27.02	2:53	"	26.73
2:22	"	27.01	2:54	"	26.72
2:23	"	27.00	2:55	"	26.71
2:24	"	26.99	2:56	"	26.70
2:25	"	26.99	2:57	"	26.69
2:26	"	26.98	2:58	"	26.68
2:27	"	26.97	2:59	"	26.68
2:28	"	26.96	3:00	"	26.68
2:29	"	26.95	3:01	"	26.67
2:30	"	26.94	3:02	"	26.67



Table I cont.

Time	Rate	e. m. f.	Time	Rate	e. m. f.
3:03	stop	26.66	3:47	4 drops a	26.77
3:04	"	26.65	3:48	min.	26.78
3:05	"	26.64	3:49	"	26.77
3:06	"	26.64	3:50	stop	26.80
3:07	"	26.64	3:51	"	27.01
3:08	"	26.63	3:52	"	27.07
3:09	"	26.62	3:53	"	27.14
3:10	"	26.61	3:54	"	27.18
3:11	"	26.60	3:55	"	27.22
3:12	"	26.59	3:56	"	27.25
3:13	"	26.58	3:57	"	27.27
3:14	"	26.57	3:58	"	27.28
3:15	"	26.56	3:59	"	27.28
3:16	"	26.56	3:60	"	27.28
3:17	"	26.56	4:01	"	27.29
3:18	"	26.53	4:02	"	27.29
3:19	"	26.53	4:03	"	27.28
3:20	"	26.52	4:04	"	27.28
3:21	"	26.52	4:05	"	27.27
3:22	"	26.50	4:06	"	27.27
3:23	"	26.50	4:07	"	27.26
3:24	"	26.50	4:08	"	27.25
3:25	"	26.49	4:09	"	27.25
3:26	"	26.47	4:10	4 drops	27.01
3:27	"	26.48	4:11	"	26.80
3:28	"	26.47	4:12	"	26.78
3:29	"	26.46	4:13	"	26.75
3:30	"	26.45	4:14	"	26.75
3:31	"	26.45			
3:32	"	26.44			
3:33	"	26.43	9:48	"	26.80
3:34	4 drops	26.50	10:00	"	26.79
3:35	a min.	26.70	10:15	"	26.79
3:36	"	26.77	10:23	1 drop	26.80
3:37	"	26.77	10:24	"	26.80
3:38	"	26.77	10:25	"	26.81
3:39	"	26.77	10:26	"	26.81
3:40	"	26.77	10:27	"	26.81
3:41	"	26.77	10:28	"	26.82
3:42	"	26.77	10:29	"	26.81
3:43	"	26.78	10:30	"	26.82
3:44	"	26.78	10:31	"	26.82
3:45	"	26.78	10:32	"	26.82
3:46	"	26.77	10:33	"	26.82

Table I cont.

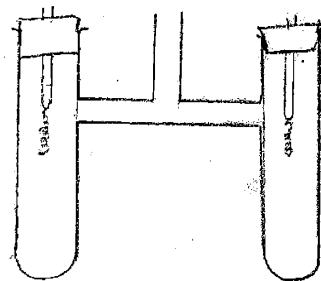
Time	Rate	e.m.f.	Time	Rate	e.m.f.
10:34	1 drop	26.83	11:44	2 drops	26.81
10:35	"	26.83	11:45	"	26.82
10:36	"	26.84	11:46	"	26.82
10:37	"	26.84	11:47	"	26.82
10:38	"	26.85	11:48	"	26.82
10:39	"	26.86	11:49	"	26.82
10:40	"	26.86	11:50	"	26.82
10:41	"	26.86	11:51	"	26.82
10:42	"	26.87	11:52	"	26.82
10:43	"	26.87	11:53	"	26.82
10:44	"	26.88	11:54	"	26.82
10:45	"	26.88	11:55	"	26.82
10:46	"	26.88	11:56	"	26.82
10:47	"	26.89	11:57	"	26.82
10:48	"	26.89			
10:49	"	26.89			
10:50	"	26.89	10:13	4 drops	26.75
10:51	"	26.90	10:45	"	26.75
10:52	"	26.90	10:55	3 drops	26.76
10:53	"	26.90	10:56	"	26.76
10:54	"	26.90	11:10	"	26.76
10:55	"	26.91	11:30	"	26.76
11:12	4 drops	26.79	12:15	"	26.75
11:13	"	26.79			
11:14	"	26.77			
11:15	"	26.78	1:00	5 drops	26.76
			2:15	"	26.75
			2:20	"	26.77
11:31	2 drops	26.80			
11:32	"	26.80	10:53	6 drops	26.80
11:33	"	26.80	10:58	"	26.80
11:34	"	26.80	11:15	"	26.79
11:35	"	26.80	11:45	"	26.80
11:36	"	26.80	11:55	"	26.80
11:37	"	26.80	12:00	streaming	26.73
11:38	"	26.80	3:15	4 drops	26.77
11:39	"	26.81	3:35	"	26.78
11:40	"	26.81	4:10	7 drops	26.76
11:41	"	26.81	4:30	"	26.73
11:42	"	26.81	4:45	"	26.73
11:43	"	26.81	4:55	"	26.70
			5:00	streaming	26.71

From these experimental data we see that when the flow was stopped, the electromotive force rose until it reached a maximum and then it fell gradually, passing its normal value, and going lower as time went on. When the flow was started again it got back to 26.77 mv. very quickly, maintaining the value 26.77 mv. as long as the rate was uniform. When the flow was stopped again, the electromotive force rose again but to a different maximum this time. The maximum value in the first case was 27.10 mv. and in the second case was 27.29 mv. The maximum reached in this way is evidently an uncertain value. When the flow was stopped, it corresponded to the experimental conditions of Lewis<sup>23</sup>'s intermittent flowing junction. My data seem to show that an intermittent flowing junction will not give a surface of contact well defined enough to be reproducible, and further it changes with the time.

The question why the electromotive force rose right after the stop of the flow cannot be explained at the present time. If the change of the electromotive force is due to diffusion, there is just as much chance for it to lower as to rise.

To find out the cause of this rise of electromotive force, a separate experiment was performed.

The tube in the form of H was filled with .1 n KCl on both sides. A pair of Ag AgCl electrodes were dipped into the solution. The potential difference between the electrodes was zero. Then a drop of KOH was introduced at the middle. The potential difference immediately rose .1 mv. and later dropped to -.27 mv.



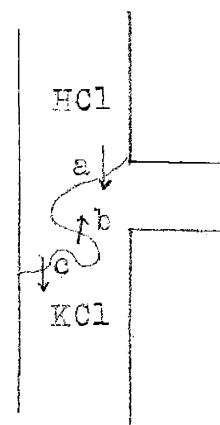
Now if the drop of KOH was perfectly symmetrical, and the surface of contact between the KOH and KCl was uniformly well defined all around the whole sphere, the liquid potential at "a" would be equal and opposite to that at "b", and the electromotive force of the cell ought to be zero. But the chances are that the drop of KOH was not symmetrical, and one side of the drop had a sharper boundary than the other. We have found that liquid potential depends upon the sharpness of the boundary. It was highly possible that the liquid potential at "a" was less than that at b or vice versa, due to the different sharpness of the boundaries "a" and "b".

KCl a KOH b KCl

KCl a KOH b KCl

In the measurement of liquid potential between

.1 n HCl and .1 n KCl, when the flow was stopped, we had a similar irregular surface of contact, where the degree of sharpness was different at different points. The boundary might assume some shape as shown in the diagram. If the surfaces at a and c are sharper than at b, then the liquid potential is going to be higher than the normal value. The arrows indicate the directions of the current.



As we examine our data in Table I, we also notice that in case the flow was stopped, after the maximum was passed, it always dropped slowly but steadily.

25                      26                      27  
 Cumming, Chanoz and Bjerrum also found that liquid potentials change with time. It is nothing more than to be expected, for the hydrochloric acid always has the tendency to diffuse into the potassium chloride side where the concentration of hydrochloric acid is zero, and the potassium chloride always tends to diffuse into the hydrochloric acid side where the concentration of potassium chloride is zero. After some diffusion has taken place the osmotic force acting on the ions at the junction will be decreased,

and the average mobilities of the ions on both sides are less different. Consequently the liquid potential decreases. If sufficient time is allowed, the diffusion approaches a limit when the compositions of both sides of the junction are half of hydrochloric acid and half of potassium chloride. Then the liquid potential will be zero.

If we plot time as the abscissa and electromotive force as the ordinate, we will have a curve for each rate of the flow, as shown on next page.

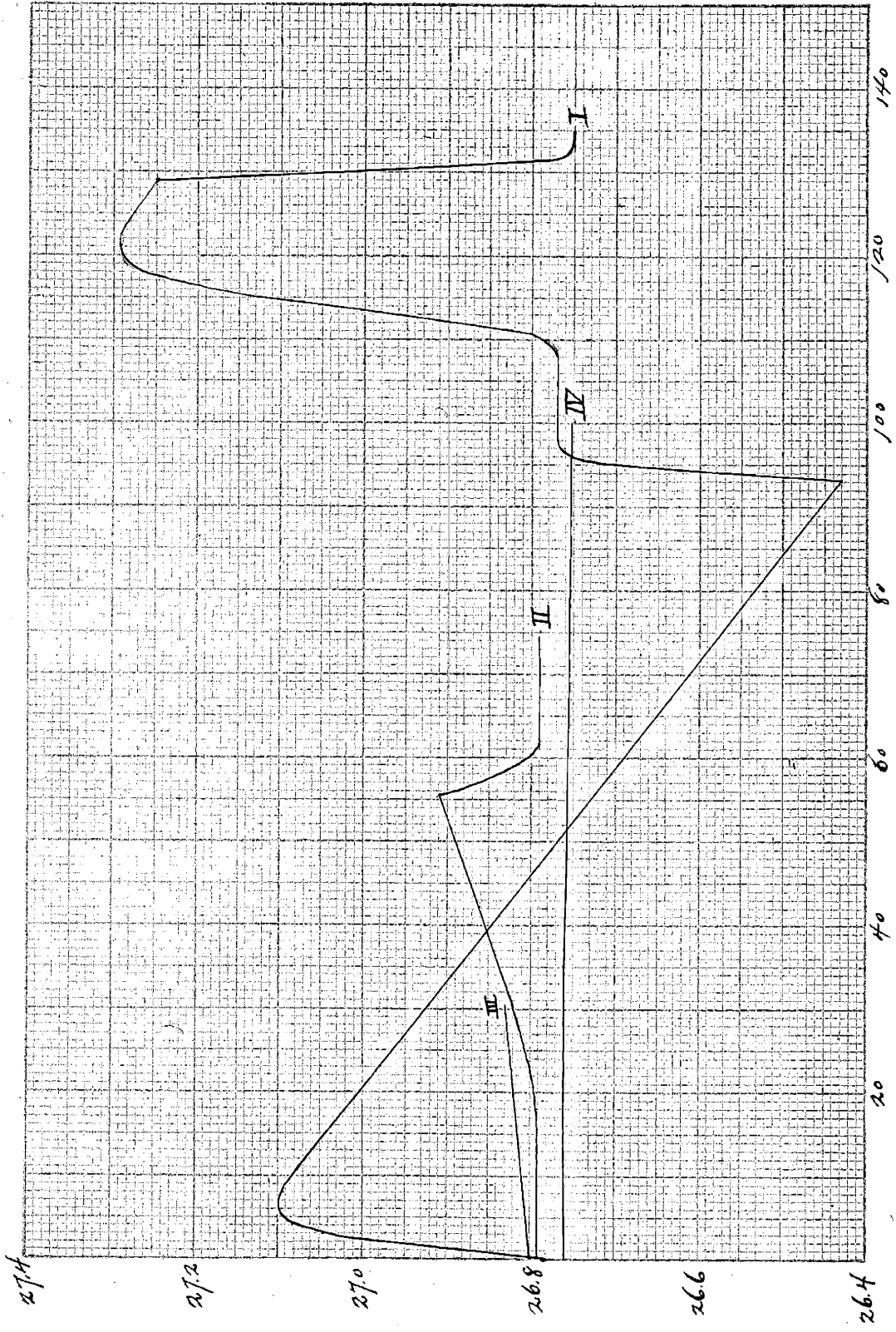
The fact that liquid potential does not change with time, if the condition of the junction is kept right, is shown by the curve I. Every time the solutions were allowed to flow the liquid potential always went back to approximately the same value. The same fact is also shown in curve IV, V and VI.

When the rate was one drop a minute, the liquid potential rose, just as when the flow was stopped, only to a smaller extent. When the rate was two drops a minute, the rise of liquid potential was so slight that one cannot tell whether it was an experimental error or a real rise of the liquid potential. When the rates were three, four, five and six drops a minute, the curves were straight horizontal lines showing that at those rates liquid potential is independent of time. With my apparatus the outlet of which was

5 mm. in diameter, these rates, from 2 drops a minute to 6 drops a minute, were the most favorable. The surface contact of the solutions at those rates were probably the sharpest. With some other apparatus the most favorable rates would possibly have a different range.

When the rate was increased to 7 drops a minute, the liquid potential began to show a decrease. The liquid potential, when the flow was streaming, was also below normal. The condition of the junction at rates higher than seven drops a minute was probably rough and ill defined, or possibly some ions actually got into the opposite side of the junction.

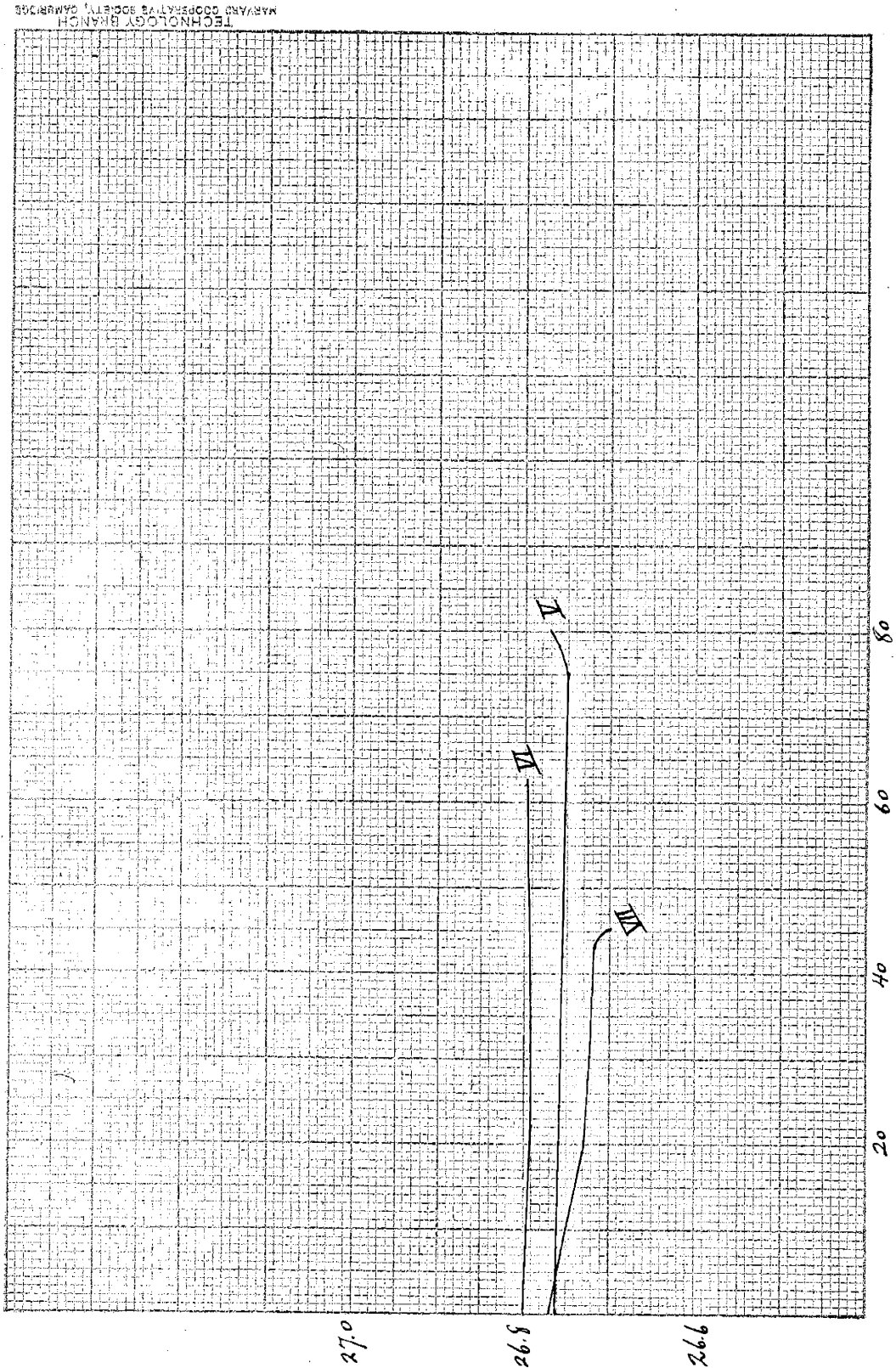
In the photograph, Figure 3 shows the sharpness of the boundary when the flow was at the rate of 5 drops a minute. Figure 4 shows the haziness of the boundary corresponding to conditions after the flow was stopped for sometime. On one side of the junction we had an alkaline solution and on the other side we had dilute phenol phthalein solution. It exhibited a red boundary surface.



EMF in mV

Time in minute





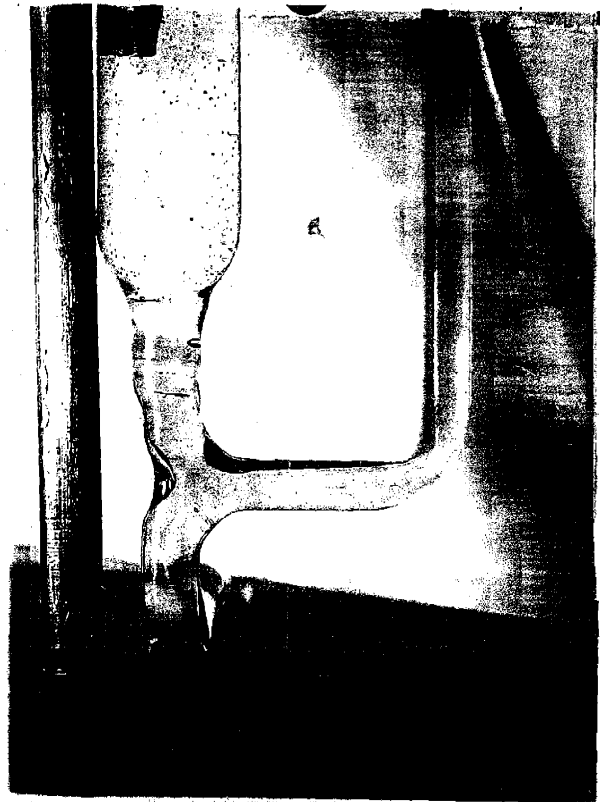
*Time in minutes*

EMF in mV

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MARYLAND COOPERATIVE SOCIETY, CAMBRIDGE



*Fig 3*



*Fig 4*

#### 4. PREPARATION OF MATERIAL:

The hydrochloric acid was prepared by the constant boiling point method of Herlett<sup>31</sup>. It has been carefully analyzed and checked by several members of the laboratory. The concentrated acid was diluted by weight with freshly distilled water to .1 molal HCl per 1000 grams of water, and to .01 molal HCl per 1000 grams of water.

The sodium chloride and potassium chloride were of the Kalbaum preparation, five times recrystallized and fused. One tenth normal and .01 normal solutions were prepared by directly weighing the salts and water.

The ammonium chloride was of the Kalbaum preparation resublimed. A concentrated solution was prepared, analyzed and diluted to .1 normal and .01 normal.

The lithium chloride was purified by Mr. Beattie. A concentrated solution was made, analyzed and diluted to .1 normal and .01 normal.

Pure caesium chloride was made by driving off the ~~chloride~~ from caesium dichloro iodide. Caesium chloride was obtained by passing chlorine into a hot solution of iodine and caesium ammonium sulphate. When the solution was cooled, the long orange needles of caesium chloriodide appeared. It was recrystallized

many times before the iodine<sup>chloride</sup> was driven off. A .01 normal solution was prepared by diluting the analyzed concentrated solution.

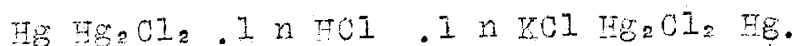
## 5. EXPERIMENTAL RESULTS.

As has been stated, the cells measured were of the type:



The electromotive force of the cells similar to the above one, with all possible combinations of two of the following, HCl, KCl, NaCl, LiCl, NH<sub>4</sub>Cl, CsCl, were measured with the Leeds and Northrup potentiometer, with all the precautions previously enumerated. The extended wire of the potentiometer was frequently calibrated and the standard cell frequently checked against others. The thermostat was kept at 25°C ± .01°C.

The liquid potential between .1 n HCl and .1 n KCl has been an object of discussion by many investigators. G. N. Lewis<sup>23</sup> found it was 28.40 mv. But in his later calculation<sup>23</sup> he has used the value 27.78 which was found by Meyer and Acree<sup>21</sup> who measured the cell



As I have pointed out before, their results showed a variation of .5 mv. due both to the

crudeness of the liquid junction and the use of calomel electrode with .1 normal HCl. Not much emphasis can be given to this value.

Lewis did not give much details as to how he obtained the value 28.40 except showing that it agreed with the value calculated from his formula with equivalent conductance data.

The value 26.78 mv. has been reproduced by me within .05 mv. more than ten times with different apparatus, new solutions and a KCl solution prepared by C. R. Park, in order to eliminate the personal equation. I feel confident that it can be reproduced with the same accuracy at any time under the same experimental conditions. It is a perfectly definite value.

Once I tried to use .1 n HCl and 1 n KCl saturated with precipitated Ag Cl and obtained the values 28.23 mv. and 28.37 mv. Upon further consideration it seems hardly fair to have the solutions saturated with precipitated Ag Cl which is an entirely different substance from the Ag Cl on the electrodes. The precipitated Ag Cl has different solubility and different free energy of formation from those of the electrolytic Ag Cl as found by T. W. Richards. The difference between 28.30 and 26.78 is 1.52 mv. In case the solubility of the precipitated Ag Cl in HCl is different from its solubility in KCl solution, we can calculate how much difference is re-

quired in order to produce a concentration cell effect of 1.52 mv., from this equation

$$E = T_{Ag} \frac{RT}{F} \ln \frac{C_{Ag} Cl_1}{C_{Ag} Cl_2}$$

$\frac{C_{AgCl_1}}{C_{AgCl_2}}$  comes out to be 1.138 which is not at all unlike the case. Therefore it is not advisable to saturate the solution with Ag Cl. All that is necessary is to have the Ag AgCl electrode, in equilibrium with the chloride solution immediately surrounding it, saturated with AgCl actually dissolved from the electrode. It does not take much time to attain this condition. The results of the electromotive force measurements of cells of all other combinations are tabulated in Table II. These represent the liquid potentials without involving the electrode potentials, since the activities of the chloride ions in equilibrium with the electrodes are in all probability equal no matter what cations are associated with them. This has been shown by Professor MacInnes<sup>30</sup> and Chow<sup>33</sup>, and proved by myself as described in another part of this thesis.

The first column shows the electrolytes whose liquid potentials were measured. The second column gives values calculated from the simplified Planck's equation

$$E = \frac{RT}{F} \ln \frac{\Lambda_{O_1}}{\Lambda_{O_2}}$$

where  $\Lambda_0$  represents the equivalent conductance at zero concentration.  $\Lambda_0$  of HCl, KCl, NaCl at 25° are taken from Noyes and Falk's article, i.e. 426.0, 150.6, 127.0 respectively. The  $\Lambda_0$  of LiCl and NH<sub>4</sub>Cl at 25° are calculated from  $\Lambda_0$  at 18°C found in Noyes and Falk, with the aid of the temperature coefficients of the ions found in Noyes and Sherrill.  $\Lambda_0$  LiCl = 114.9,  $\Lambda_0$  NH<sub>4</sub>Cl = 150.2 at 25° C. The  $\Lambda_0$  of CsCl at 25°C is found in Landolt and Börnstein, i.e. 153.5.

The third and sixth columns represent the values directly determined by experiments. Nearly all measurements have been repeated three times and the difference seldom exceeds .1 mv. Considering that the electrodes often differ by more than .05 mv., the variation due to the liquid potential is very small.

The fifth and the eighth columns represent values calculated from the Lewis modified formula of Planck

$$E = \frac{RT}{F} \ln \frac{\Lambda_1}{\Lambda_2}$$

where  $\Lambda$  stands for the equivalent conductance of the solutions at the concentration actually employed. These values are found in Noyes and Falk's article

	.1 n	.01 n
HCl	390.4 ✓	411.6 ✓
KCl	129.0 ✓	141.4 ✓
NaCl	106.8 ✓	118.7 ✓
LiCl	93.8	108.3
NH <sub>4</sub> Cl	130.	140.7

91.97  
122.5

TABLE II

Electrolytes	Planck .1 n	Observed n	By addition with Arbitrary Scale	Lewis	Observed .01 n	By ad- dition	Lewis
HCl KCl ✓	26.73	26.78	<u>35.65</u> 8.87 26.78	28.47	25.70 25.75 25.72 25.73	<u>33.75</u> 8.20 25.55	27.41
HCl NaCl ✓	31.12	33.07 33.13 33.07	<u>35.65</u> 2.56 33.09	33.33	31.12 31.19 31.18	<u>33.75</u> 2.63 <del>33.75</del>	32.05
HCl LiCl ✓	33.69	34.87 34.87 34.83	<u>26.78</u> 8.87 35.65	36.64	33.77 33.79 33.70	33.75	34.25
HCl NH <sub>4</sub> Cl ✓	26.80	28.40 28.39	<u>35.65</u> 6.77 28.88	28.37	27.06 27.00 27.00	<u>33.75</u> 6.89 26.86	27.60
KCl NaCl ✓	4.38	6.45 6.35 6.45	<u>8.87</u> 2.57 6.30	4.86	5.65 5.65	<u>8.20</u> 2.63 5.57	4.54
KCl LiCl ✓	6.96	8.85 8.63 8.89	8.87	8.19	8.25 8.16 8.20	8.20	6.89
KCl NH <sub>4</sub> Cl ✓	.07	2.13 2.16 2.20	<u>8.87</u> 6.77 2.10	.08	1.30 1.31	<u>8.20</u> 6.89 1.31	.18
NaCl LiCl ✓	2.57	2.65 2.65 2.57	2.57	3.34	2.65 2.57 2.67	2.63	2.26
NaCl NH <sub>4</sub> Cl ✓	-4.31	-4.21 -4.26 -4.15	<u>2.57</u> 6.77 -4.20	-4.94	-4.31 -4.21	<u>2.63</u> 6.89 -4.26	-4.41
LiCl NH <sub>4</sub> Cl ✓	-6.89	-6.93 -6.92	-6.77	-8.27	-6.89 -6.89	-6.89	-6.72
CsCl LiCl ✓	12.66				7.78 7.81	7.80	
CsCl NaCl ✓	4.87				5.40 5.41 5.36	7.80 -2.57 5.23	
CsCl KCl ✓	- .49				- .30 - .32	7.80 8.16 - .36	
CsCl NH <sub>4</sub> Cl ✓	.56				.95	7.80 6.89 .91	
CsCl HCl ✓	-26.24				-24.85	7.80 33.70 -25.90	



Columns four and seven show the additive relations of liquid potential values. If we arbitrarily assign a certain number to each electrolyte at a definite concentration, these numbers being derived from a few measurements, we can calculate the liquid potentials of all possible combinations. To illustrate the point let us utilize our figures and show how columns four and seven are obtained. From direct measurement we found that the liquid potential between .1 n KCl .1 n LiCl was 8.87 mv. To have a starting point in the scale let us assign zero to LiCl for LiCl among all other chlorides has the lowest equivalent conductivity. Then KCl at .1 normal is naturally 8.87. From direct measurement we also know that the liquid potential between .1 n HCl .1 n KCl is 26.78 mv., and the current flows from HCl to KCl. Since KCl is higher than LiCl in the scale of number by 8.87, and HCl is higher than KCl by 26.78; then HCl is higher than LiCl by 35.65. Let 35.65 be the number assigned to HCl. The liquid potential between .1 n NaCl .1 n LiCl is 2.57 mv., between .1 n NH<sub>4</sub>Cl .1 n LiCl is 6.77 mv. Let 2.57 be the number for NaCl and 6.77 for NH<sub>4</sub>Cl. Then we will have the following complete scale. The scale for .01 normal solution is obtained in a similar manner.

	.1 normal	.01 normal	
LiCl	0	0	
KCl	8.87	8.20	
HCl	35.65	33.75	33.82
NaCl	2.57	2.63	
NH <sub>4</sub> Cl	6.77 692	6.89	
CsCl		7.80	

Suppose we want to find out what the liquid potential between .01 n. KCl .01 n NH<sub>4</sub>Cl should be without determining it. Take the number for KCl 8.20, and subtract from it the number for NH<sub>4</sub>Cl 6.89 and get 1.31. Since the number for KCl is greater than that for NH<sub>4</sub>Cl, we can predict that the current is going to flow from the KCl to the NH<sub>4</sub>Cl. Experiment fulfilled the expectation in magnitude and direction. This method of calculation agrees very well with experiments in all cases except four, namely .1 n HCl .1 n LiCl, .1 n HCl .1 n NH<sub>4</sub>Cl, .01 n HCl .01 n NaCl, and .01 n HCl .01 n CsCl. This is at the present time the only method that meets with partial success. We should not be surprised to find that the experimental results agree neither with Planck's nor with Lewis' equations, since I have pointed out the various imperfections of their assumptions at the former part of this thesis.

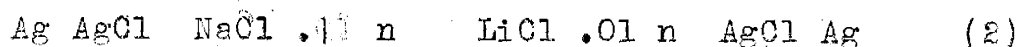
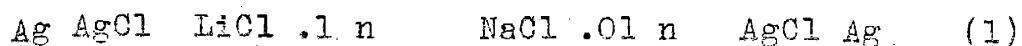
There are a few peculiarities in Table II that are worth noticing

		Planck	<i>obs.</i>	
			.1 n	.01 n
NaCl	LiCl	2.57 mv.	2.62	2.63
NaCl	NH <sub>4</sub> Cl	-4.31	-4.21	-4.26
LiCl	NH <sub>4</sub> Cl	-6.89	-6.92	-6.89

This is abstract from Table II. We see that all these experimental values agree with Planck's calculated values almost perfectly. Are NaCl, NH<sub>4</sub>Cl, LiCl completely ionized as Planck assumed? The very fact that the values at .1 normal are almost the same as those at .01 normal seems to further support this assumption. On the other hand outside of these three combinations the phenomenon was not duplicated. It is not at <sup>all</sup> impossible that the ionizations or mobilities of the ions of these electrolytes change in such way that the ratio of their equivalent conductances remain approximately constant, as the concentration changes from .1 normal to .01 normal

6. THE ACTIVITIES OF THE CHLORIDE  
IONS IN SODIUM CHLORIDE  
AND IN LITHIUM CHLORIDE  
SOLUTIONS.

This part of the research consists in measuring the electromotive forces of the following cells



As usual the electromotive force of cells of this type come from three sources, namely the two electrode potentials and the liquid potential between the solutions. What we measure is the sum of the three electromotive forces. If we subtract the liquid potentials from the measured electromotive forces, the differences will represent the electrode potentials. Other parts of this research show that the liquid potentials between Li Cl and NaCl both at .1 normal and .01 normal do obey the Planck equation very well. That gives me confidence to calculate the liquid potentials involved in the above two cells by the Planck's equation.

Leaving the liquid potential in care of Planck's equation, let us consider the changes in state at the electrodes, when one faraday of electricity passes

through the cell. In cell (1) one equivalent of chloride ion disappears at Li Cl .1 n and one equivalent of chloride ion appears at Na Cl .01 n. In cell (2) one equivalent of chloride ions disappears at NaCl .1 n and one equivalent of chloride ion appears at Li Cl .01 n. Therefore the free energy changes attending such changes of state are

$$\begin{aligned}
 (1) \quad -\Delta F &= E N F = RT \log_e \frac{A_{Cl(.1 n LiCl)}}{A_{Cl(.01 n NaCl)}} \\
 &= RT \ln \frac{.1 a_{Cl(.1 n LiCl)}}{.01 a_{Cl(.01 n NaCl)}} \\
 &= RT + RT \ln \frac{a_{Cl(.1 n LiCl)}}{a_{Cl(.01 n NaCl)}}
 \end{aligned}$$

$$(2) \quad -\Delta F = RT + RT \ln \frac{a_{Cl(.1 n NaCl)}}{a_{Cl(.01 n LiCl)}}$$

Thus we can calculate what the ratios of activity coefficients of the chloride ions of both salts are.

The liquid potentials are of the type of different electrolytes at different concentrations. To calculate that type of liquid potential it requires the original Planck's equation, i.e.

$$E_1 = \frac{RT}{F} \log \xi \quad \text{where } \xi \text{ is a function}$$

*defined* in the following equation.

$$\frac{\xi C_2 u_2 - C_1 u_1}{C_2 v_2 - \xi C_1 v_1} = \frac{\log \frac{C_2}{C_1} - \log \xi}{\log \frac{C_2}{C_1} + \log \xi} \quad \xi \frac{C_2}{C_1} - 1$$

$C_2, C_1$  = Concentrations of the solutions

$u_2, u_1$  = Mobilities of the cations

$v_2, v_1$  = " " " anions:

If we put

$$\frac{\xi C_2 u_2 - C_1 u_1}{C_2 v_2 - \xi C_1 v_1} = \eta$$

$$\frac{\log \frac{C_2}{C_1} - \log \xi}{\log \frac{C_2}{C_1} + \log \xi} = \frac{\frac{C_2}{C_1} \xi - 1}{\frac{C_2}{C_1} - \xi} = \eta$$

can be solved graphically by plotting  $\eta$  against  $\xi$ .

In the case of cell (1) Li .1 n NaCl .01 n

$$C_2 = .1 \quad u_2 = 39.5 \quad v_2 = v_1 = 75.4$$

$$C_1 = .01 \quad u_1 = 50.8$$

$$\frac{\xi 39.5 \times .1 - 50.8 \times .01}{.1 \times 75.4 - \xi .01 \times 75.4} = \eta$$

when $\xi$ =	.1287	1	2	2.1	2.2	3
$\eta$ =	0	.507	1.26	1.302	1.387	2.124

These values are plotted as curve I.

$$\frac{\log \frac{.1}{.01} - \log \xi}{\log \frac{.1}{.01} + \log \xi} = \frac{\frac{.1}{.01} \xi - 1}{\frac{.1}{.01} - \xi} = \frac{(1 - \log \xi)(10 \xi - 1)}{(1 + \log \xi)(10 - \xi)} = \eta$$

when $\xi$	=	.1	or 10	1	2	3	.2	.5
$\eta$	=	0		1	1.278	1.47	.576	.785

These values are plotted as curve II. Curve I and curve II intersect at a point where  $\xi = 2.09$ . Thus when  $\xi = 2.09$  it satisfies both equations.

$$E_L = \frac{RT}{F} \ln 2.09 = .0910$$

The measured electromotive force of this cell is 35.55 mv. Since the liquid potential is going in opposition to the electrode potential, the potential difference of the electrodes is 35.55 mv. + .01910 = 54.65 mv.

In the case of cell (2) NaCl .1 n LiCl .01 n we have

$$\frac{\xi 5.08 - .395}{7.54 - .754 \xi} = \eta$$

when $\xi$	=	.0779	.1	1.0	2	1.5
$\eta$	=	0	.01515	.691	1.62	1.125

These values are plotted as curve III, which intersects curve II where  $\xi = 1.55$

$$E_L = \frac{RT}{F} \ln 1.55 = .01122 \text{ volts.}$$

The measured electromotive force of the cell is 43.55 mv. Therefore the potential difference between the electrodes is 43.55 + 11.22 = 54.77 mv. which agrees very well with cell (1) within experimental error and electrode variation.

From these values we can get the ratios of the chloride ion activity coefficient

$$\frac{a_{\text{Cl}}(.01 \text{ n NaCl})}{a_{\text{Cl}}(.1 \text{ n LiCl})} = 1.186$$

$$\frac{a_{\text{Cl}}(.01 \text{ n LiCl})}{a_{\text{Cl}}(.1 \text{ n NaCl})} = 1.192$$

The difference is less than one percent.

$$\frac{a_{\text{Cl}}(.01 \text{ n NaCl})}{a_{\text{Cl}}(.01 \text{ n LiCl})} \times \frac{a_{\text{Cl}}(.1 \text{ n NaCl})}{a_{\text{Cl}}(.1 \text{ n LiCl})} = \text{nearly to unity,}$$

or to be exact .9955. That can be easily accounted for by accepting Professor MacInnes' theory that the activities of the chloride ions are equal at the same concentration no matter what cations are associated with them. On the other hand if we accept the other alternative that the chloride ion activity in .01 n NaCl is not equal to, but greater or less than the chloride ion activity in .01 n LiCl, then the activity of chloride ion activity in .1 n NaCl must be less or greater than the chloride ion activity in .1 n LiCl by such an amount that ratio of the product

$$\frac{a_{\text{Cl}}(.01 \text{ n NaCl})}{a_{\text{Cl}}(.01 \text{ n LiCl})} \times \frac{a_{\text{Cl}}(.1 \text{ n NaCl})}{a_{\text{Cl}}(.1 \text{ n LiCl})}$$

remain unity. Since this is very improbable, we can safely conclude that the chloride ions in .1 n LiCl



have the same activity as in .1 n NaCl, and the chloride ions in .01 n LiCl have the same activity as in .01 n NaCl.

I wish to take this opportunity to thank Dr. MacInnes for his constant attention and interest on the problem during the investigation.

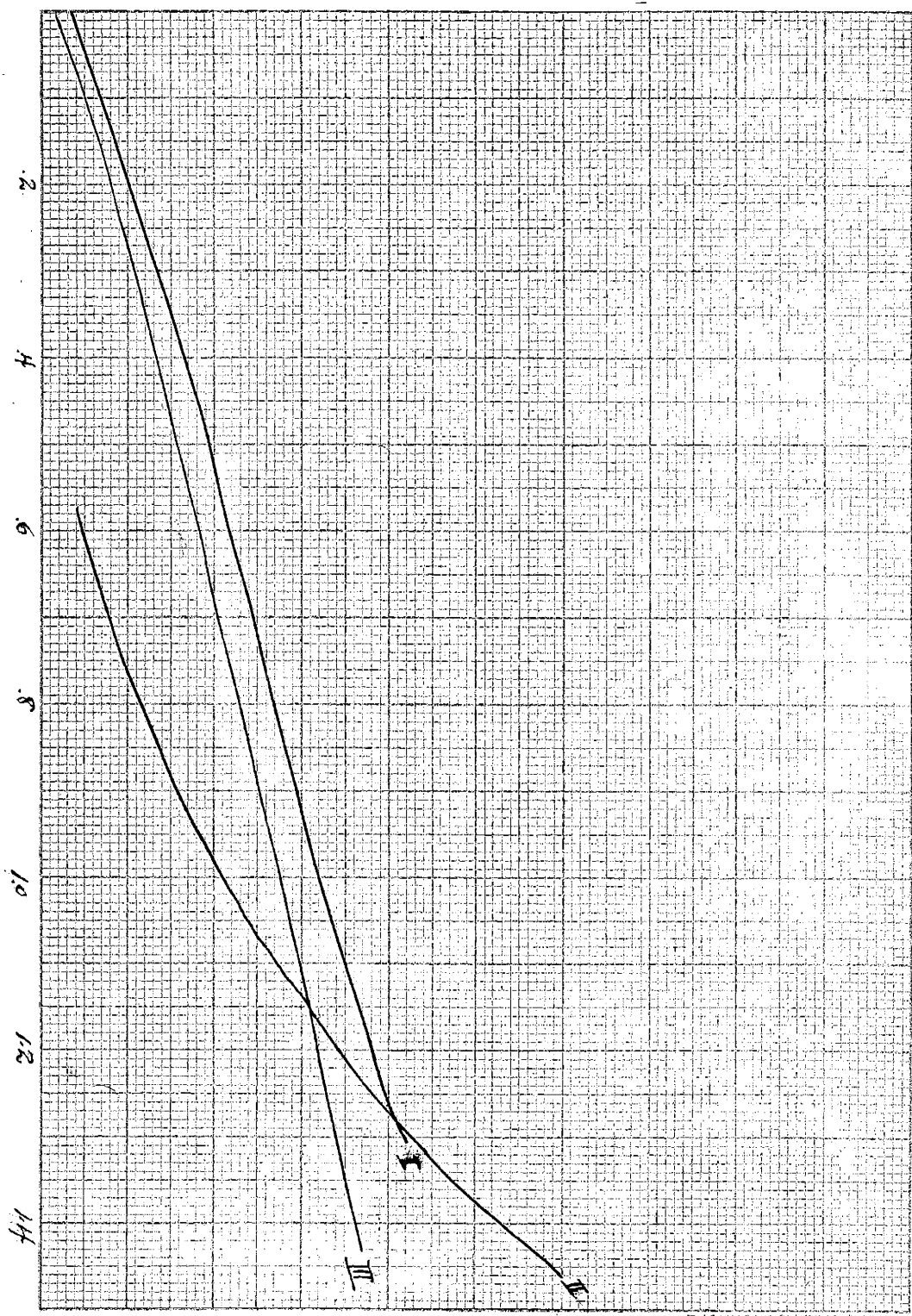
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